REFINER
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A Battle Half Won . . .

IT is incumbent upon the petroleum industry to push through a nationwide program of gasoline tax reduction. Unless this is done the industry stands to lose by the efforts made thus far of giving the public information on the tax burden. So far the owner of an automobile has been made conscious of the fact that he pays the most severe tax ever saddled on a commodity when he buys gasoline. Under that knowledge his reaction will be to restrict the use of his automobile.

This automobile owner must now be encouraged to throw the weight of his ballot into a campaign that will reduce taxes. The only escape is through the election of state legislators who are pledged to reduce these taxes. For that reason the petroleum industry must have a sensible program. It should include:

A state tax of not more than three cents per gallon.

No assessment by the federal government.

All funds restricted to highway purposes.

Correction of the agricultural exemption farce.

Reduced automobile license fees.

Facts are so plentiful in defense of this program that they need no recital. They are known to the industry, to other industries and, best of all, to the public.

In several states, Colorado, Oklahoma and Indiana, concerted drives are under way to bring about programs of this nature. They will be fought through in the political campaigns of this summer. Unfortunately the political arena is the only chance to defeat the taxation of gasoline, which has become little short of a legislative racket.

By every means at its disposal the petroleum industry should place its program before the voters of the nation. No refining concerns should seal a piece of first-class mail without inclusion of its position on gasoline taxes. Jobber customers should be encouraged to pass this information along to customer. Concerns with retail outlets have the choice method of reaching the public.

One chance that is rarely used is advertising. Newspaper space has long been accepted as the quickest and surest means of gaining public approval. Seldom, however, does the petroleum industry use this for waging its tax battle. Gasoline can be sold while the facts about gasoline taxes are being told. In that way the effort to reduce gasoline taxes can be pitched on a high plane.

Gasoline taxes are but a part of the excessive tax burden borne by the American public today. It would be well if the industry enlarged its campaign of publicity to include that of uniform reduction in the cost of government. The American people are today compelled to divert $14,000,000,000 of annual income to defray the cost of all government. The status of commerce and wages will not meet this call. Reduction will come either through order or through ruin.

When the Congress of the United States can find means of reducing the cost of federal government by only $165,000,000 for a year, it is time for the ballot to assert itself by replacing those who decline to match private economy with governmental economy.

Above all it is time to replace men who are schooled in the thought that highway expenditures must increase each year, despite reduced costs of material and labor, who consider gasoline the product to attack when some other source of revenue fails, who look upon the petroleum industry as spineless and unworthy.

Gasoline taxes can be corrected but only the petroleum industry can assure it.

▼ ▼ ▼

Control of High Pressure Cracking Stills

G. VANDENBERG
Designing Engineer

REPLACING manual control, automatic remote control instruments govern the operation of cracking stills more efficiently, more reliably and more safely.

To get the most out of a system of control, it should indicate and/or record all pressures, temperatures and quantities. The quantities to be measured are those of all materials involved in the process; fresh charge, circulating oil, reflux, distillate, fixed gas, and fuel. All of these can be measured by orifices. The measurements of far-off orifices are electrically relayed to the control board and there indicated and recorded to the end that a complete bookkeeping system is displayed on the board. The combustion process is handled in a similar manner, and admission of fuel (gas or oil) must be regulated from the board. At the same time the quantity of fuel consumption is measured, the quantity charged to the cracking tubes, the oil and furnace temperatures at vital points, CO_2 and draft or pressure; everything, in fact, necessary to scientific regulation of the cracking operation and combustion.

The cracking furnace always requires the closest attention because it is the heart of the cracking installation, operates at the highest temperature and pressure, and comprises the greatest hazard. Reliable distant control is more essential here than at any other portion of the system. Figure 1 represents an arrangement of Tube and Tank cracking installation with remote control, and is similar in design to a system now in operation nearly two years without accident. Four cracking

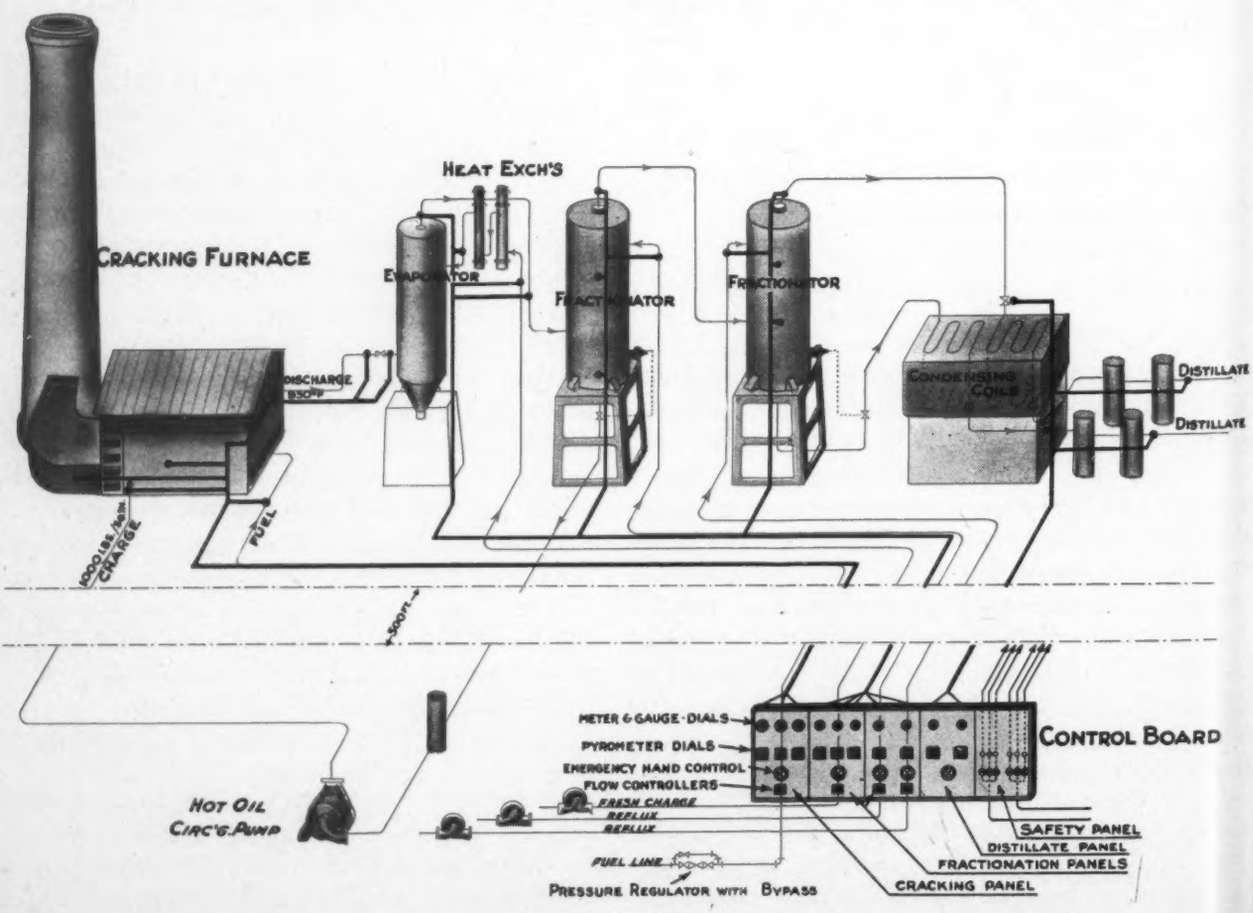


FIGURE 1—*Remote Controlled Cracking Still*

stills of 3000 barrels capacity each are combined and controlled from one board, making possible the operation of two units by one operator. Two sets of four stills are operated in this manner.

There are, of course, several viewpoints as to the set-up of a control board. The location is usually influenced and determined by the designer's idea on "safety first." It has been proven that operation at 500 feet distance is as practical as a distance of 100 feet; electric relaying making the desirable distance possible.

LOCATION OF CONTROL BOARD

The control board and the control house should be erected along the main pipe trench, or pipe trench and control house combined should be located in such manner that both form a practical layout. The low pressure end of the still is a practical location. Control of the still centers largely about the admission of charged oil, reflux, and fuel. Bringing these lines through a trench to the still and placing the control house along this trench, is one factor in determination of the location.

The selection of a suitable location and bringing the pipe trench towards the control house is another means of determining location. In some cases the control house is combined with the pump house. Some designers place the control board in the pump house, but a separate control house, containing nothing but the control board, has proven of value.

Fuel regulators should be close to the control house, placed just outside and in the pipe trench. The fact that they will sometimes get out of order requires that they must have an arangement for by-passing. The layout and installation requires much space. This, and the possibility of leakage of poisonous gases through the many flanges employed, makes it desirable to keep such equipment outside of the control house. They must be close to the control room in order that the operator may be able to operate the by-pass quickly, in case of failure of the regulator.

Fresh charge, reflux and charge to the cracking furnace (recirculating stock and fresh charge) are handled by automatic control devices. Keeping these quantities constant, by means of automatic flow controllers, for instance, makes the whole cracking still automatic. Therefore the center of automatic regulation is the flow controller which keeps the rate of charge always at the desired point. (Figure 2.)

FLOW CONTROLLER

The flow controller is a precision instrument, virtually, and gives most perfect results when attached to the discharge of a centrifugal pump, which in itself has steady flow characteristics. Maximum steady flow is secured from a centrifugal pump driven by a synchronous motor, which avoids the pulsations familiar in the operation of the duplex type pump. A twin flywheel pump also renders desirable service. A heavy flywheel, a sensitive governor and large air vessels or cushion drums are useful in minimizing irregularities. With the electrically driven centrifugal pump, a throttle on the discharge may do all the regulating without harm to pump or motor, and what is more important, it will perform with immediate response and without hunting. Many refiners prefer the duplex pump because of their simplicity, ease of repair, and stuffing boxes easier to pack, but this simplicity is accompanied by complexity of regulation. Flow controller operation is based upon the measurements of an orifice, and measurements of pulsations through an orifice lend to difficulty in securing desirable accuracy.

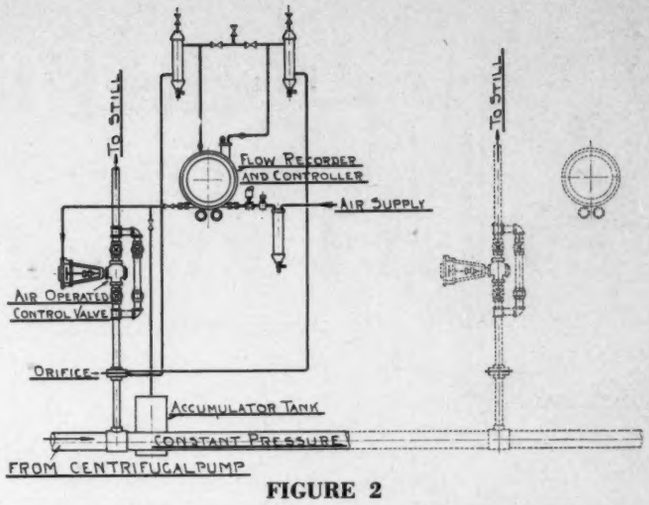


FIGURE 2

Typical Arrangement of Controllers, Controlling Charge to a Multiple of Stills from a Main Charge Line.

Flow control for a turbine driven pump is handled in the case of the electrically driven pump, by means of throttling the outlet. Constant speed, gear driven, reciprocating pumps may be controlled by a return line to the suction side of the pump and an instrumental control in this return line.

If the charge to the cracking furnace is held constant, either by sensitive pump governors or flow controllers, the automatic control of firing becomes very simple. Firing the cracking furnace is entirely different from firing the boiler, as the amount of B.t.u.'s required by the furnace is constant, and therefore the fuel supply must be constant. The difficulty with fuel supply is usually that the pressure changes too often and with too great difference between high and low pressure. Consequently one or two good regulators must be placed in the fuel line to hold the pressure constant. A throttle system, attached to the control board, will enable the operator to regulate the flame according to furnace temperature and the heated oil. This throttling by hand, by the operator, tends to make the system semi-automatic.

Thermocouples are placed in the furnace, at the place of air entrance, center of combustion or center of furnace, at the point where gasses leave the furnace and at stack entrance. Oil temperatures are measured at entrance to cracking tubes and at the point where the

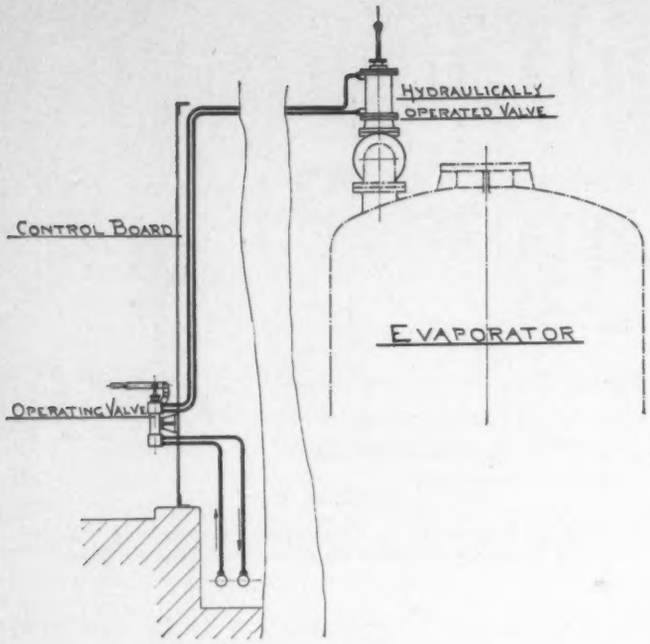


FIGURE 3
Typical Arrangement of Hydraulic Valves

oil leaves the tube. Furnaces that are divided in radiant and convection sections, and probably soaking sections, will require more thermocouples, as operators are usually interested in oil temperatures at the point where the oil leaves the respective section or tube bank. In high pressure practice the operating temperatures are found through research and long experience and it is the duty of the operator to stick to prescribed temperatures. Temperature is more important in cracking than pressure, and for that reason thermocouples are placed at every point of the furnace that may be of interest and value to the operator and to research.

Temperature regulation may be called quantity regulation, since temperatures are regulated by changing quantities of fuel, or air, of charged oil. Keeping the temperature constant means mostly keeping quantities constant that influence the temperature. In fact, the whole of regulation is a throttling affair. Knowledge of quantities involved and the change of quantities is of great importance. Orifice meters are employed to secure this knowledge. Quantities of liquid gas and steam, are all measured the same way; by measuring the pressure on both sides of an accurately machined orifice.

The EMF (voltage) of a thermocouple must be relayed to the control board without loss, and the problem is delicate since the voltage is in the range of 10 to 40 millivolt. It does not require much electrical knowledge to understand that poor connections (which cause large resistance) and outside influences like neighboring power lines and their magnetic fields, can easily cause wrong readings. A good pyrometer installation is accurate within one or two degrees. Disturbances, however, may disturb the readings to 100 degrees or more—in proportion to the reduced voltage. Therefore careful protection of pyrometer wiring is essential.

In order to secure clear vision of temperature recording instruments they should be assembled in such manner that the operator need not go through all kinds of acrobatics to see them. The last recording should be a little below eye level of the average man. Emergency hand wheels should be located "where the operators hands are." Pressure gauges may be placed a little overhead but so that they can be easily observed. Projecting instruments are more difficult to read than flush mounted dials. Flush mounted panels manufactured from substantial sheet steel, and angle iron and flush welded, make a neat board. Slate panels are objectionable because they become weak when many holes are drilled in them, while all instruments must project.

THE SAFETY PANEL

The safety panel is no less important to safe operation than the control panel. This panel is divided into two parts; one half carrying the hydraulic part, where by means of hydraulic manifolds, hydraulically operated valves at towers, furnace and pumps can be closed or opened in case of emergency; and the other half given over to steam valves, by means of which steam can be admitted to places where fires may occur. Such points are:

1. The interior of the furnaces, where tubes may split.
2. The space where tube-heads project from the heating element.
3. Pipe flanges and connections, which through vibration and other causes may begin leaking.
4. Safety valves, where emerging vapors may ignite spontaneously.
5. Stuffing boxes on the hot oil pumps.
6. Pump houses housing the charging and reflux pumps.

Hydraulic manifolds, as well as hydraulically operated valves can be purchased as standard equipment, and their description and manner of operation is found in the catalogs of the manufacturing and engineering concerns.

A safety panel must be kept in perfect working condition, for a poorly maintained panel has no value whatever. It must be of well developed design, and the same standards could be applied to it as to other fire fighting equipment that must pass underwriters approval. It must be thoroughly tested at every shut-down of the cracking unit.

The system of hydraulic operation of valves (Figure 3) and the spraying of steam into blazing places, is in itself very simple. The hydraulic system may be designed so that by operating a single valve, the entire process of cracking, distilling and pumping, is immediately halted.

The number of steam sprayers is more or less limited to enclosed places, such as the interior of the furnaces, towers, and pump houses. At points where air freely enters or circulates, a steam sprayer can only act as a preventive or cooler. Such steam lines, obviously, must be kept free of water.

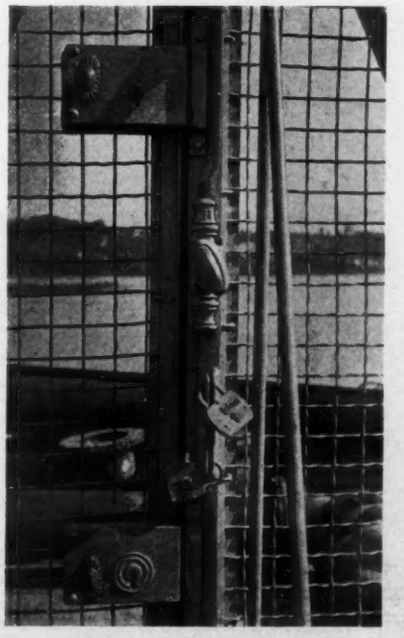
First Major Oil Refinery • Completed in France

HERBERT TRIVAL

A FEW years ago the French government decided to foster the erection of oil refineries in France, as one of the necessary branches of protection against foreign military invasion. To further this plan, the government raised the import duty on finished petroleum products, and lowered the tariff on crude oil. In addition, the government furnished financial and other forms of assistance. In turn for this assistance, the government made a ruling that 60 per cent of all material for the erection of these refineries must be of French manufacture, unless it could be proved that the necessary equipment could not be procured in France. This clause, which appears satisfactory from the general French viewpoint, is very unsatisfactory from the viewpoint of the French refiner.

In complying with this ruling, the French refiner has had to install some equipment far below the standard found in the United States. It has also caused months of delay, because the French factory manufactures only on order, and they are notoriously slow. An example is found in buying a lathe for the machine shop. The manufacturer required six moths for delivery for an ordinary type lathe. All orders for equipment had to be submitted to at least six French manufacturers. If they refused to bid on the equipment, it was then possible to place the order in some other country. All this entailed long delays.

At present four refineries are under construction in France. The Raffineries de Petrole de la Gironde at Bordeaux is completed and operating. With the exception of two or three small skimming plants built in years gone by, this is the first one completed since France decided she needed to refine her own gasoline. The plant is located on a neck of land where the rivers Garonne and Dordogne join together to make the Gironde.



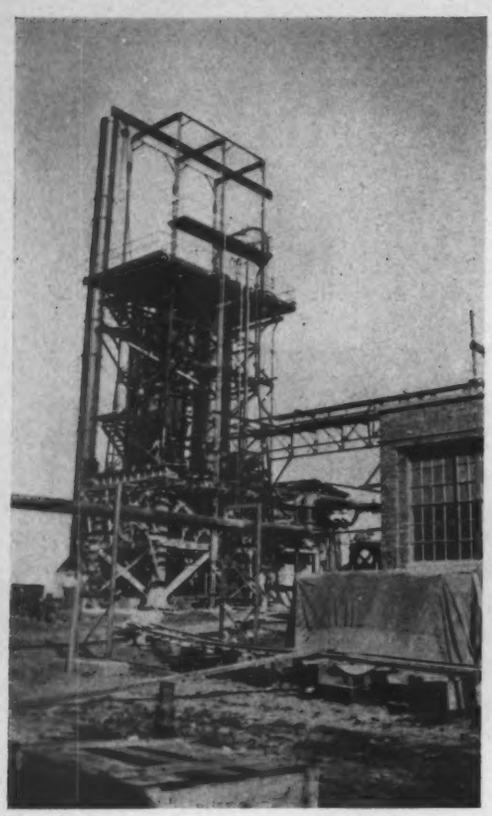
Four Locks Guard the Gate to the River Loading Dock, Raffineries de Petrole de la Gironde.

Most of this land was made by pumping out the river channels. The land is low, and water is encountered two feet below the surface. In order to secure firm foundations, it was necessary to drive wooden piles, 75 feet long, under the foundations for all heavy pieces of equipment, such as boilers, stacks, generator and towers. Foundations for buildings are shallow, but cover a large area. They are in reality mats, built of reinforced concrete.

The compressor was originally mounted in the power house, on a concrete block four feet above the ground, and two feet below. This is a French Rateau, vertical, 600 cubic feet per minute, compressor. When started, the vibration was so great, due to the nature of the ground, that it shook the whole building, and could be felt 300 feet away. This continuous vibration would have been detrimental to the electric generator, installed in the power house, so the compressor was moved to a separate building 1000 feet away.

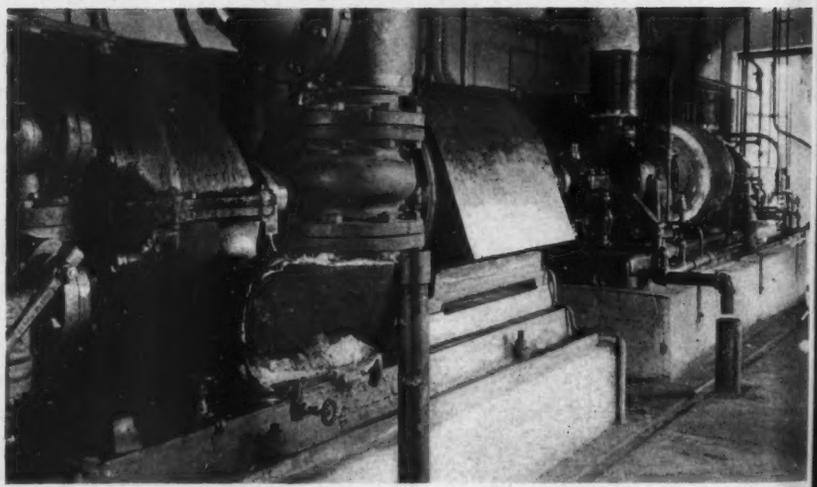
The general contract for the construction of this refinery was awarded to the Societe D'Installations Industrielles of France. This is a French subsidiary of Bethlehem Steel Company. The S. I. I. sublet all the engineering and design to various refinery engineering firms, but they erected all the units and auxiliary equipment. For cracking stills they came to two American firms. For cracking kerosene and gas oil, they erected a Cross cracking unit of 2500-barrel capacity. This is of conventional design, except that the fresh feed is fed direct to the bubble tower, thus eliminating the mix tank. The reaction chambers, of which there are two, are mounted in a horizontal position, instead of vertical. The

Raffineries de Petrole de la Gironde

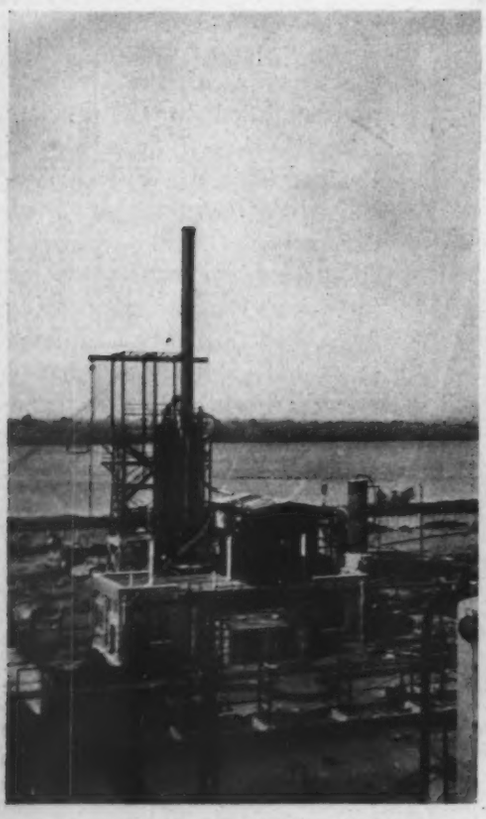


General View of the Refinery

Dubbs Cracking Unit, Above, and Below, a View of the Same Equipment from Another Angle.

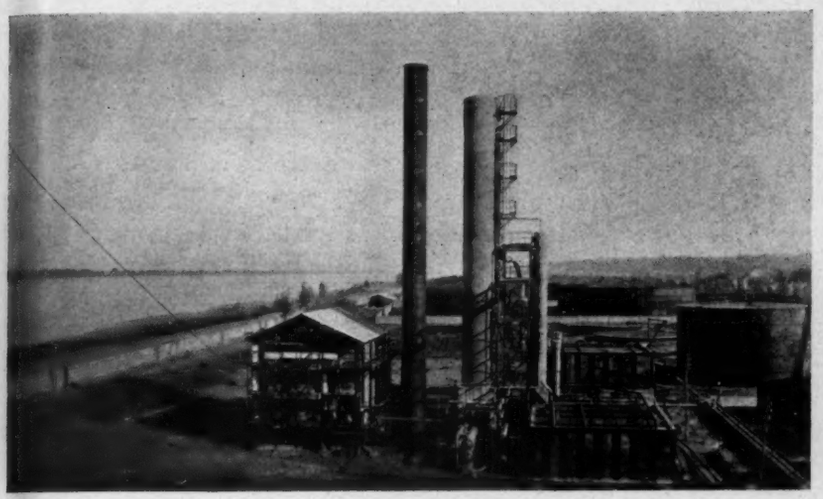


Hot Oil Charging Pumps for Cross Still. Combination Steam Turbine and Motor Drive.

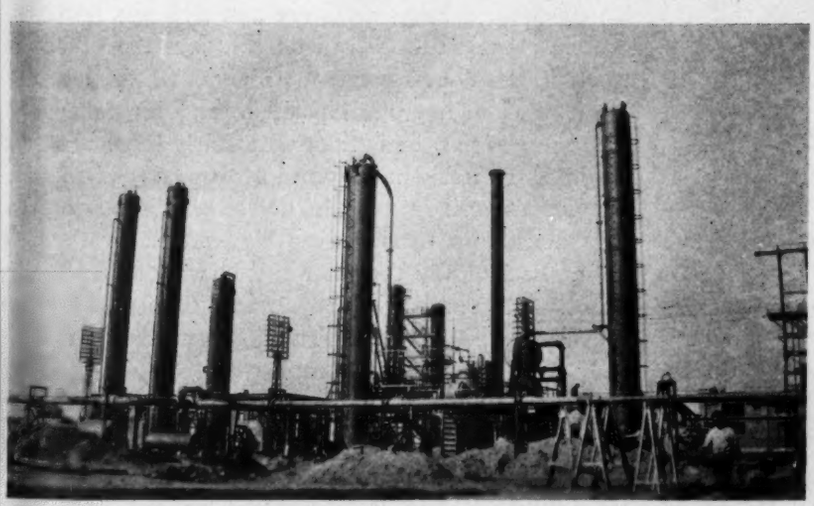


Interior of Transfer Pump House

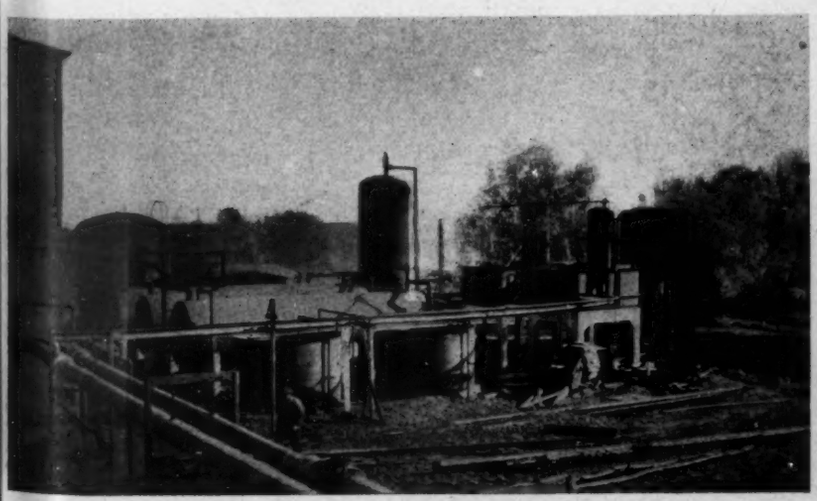
A Modern Refining Plant at Bordeux, France



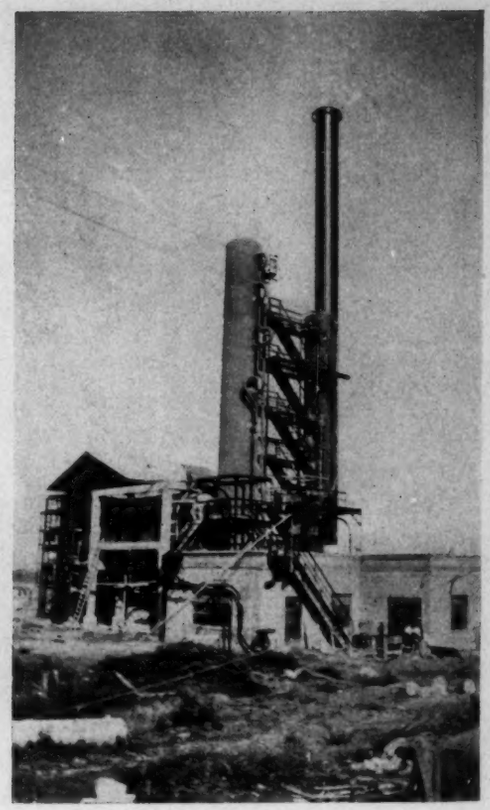
Topping Plant



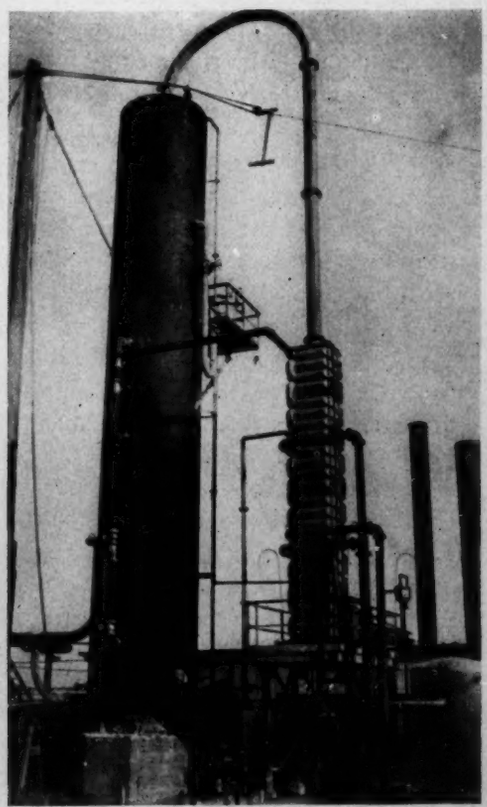
Vapor Recovery and Stabilizers; Left to Right—Gas Absorbers, Scrubber, Evaporator and Stabilizer.



Sweetening Plant



Cross Cracking Unit, Above, and Below, Tower on Re-Run Still Showing Vapor Condensers.



Pacific hot oil centrifugal charging pump has 11 impellers, and will put up a maximum pressure of 2000 pounds per square inch, at 3000 r.p.m. The pump is driven by either electric motor or steam turbine, mounted on the same shaft. If the electric current is accidentally cut off, tthe steam turbine automatically takes up the load. The motor is a 450 horsepower General Electric and the steam turbine is of the same make, with both high and low pressure turbine wheels. All bearings are lubricated by force feed, and the packing glands of the pump are water cooled. All the equipment for this still was fabricated in the United States, except the reaction chambers, which were manufactured by the German firm, Krupp.

The second cracking still is a Dubbs standard design. This still cracks the bottoms from the topping operation. It also has a capacity of 2500 barrels per day. The reaction chamber, flash dephlegmator, and main dephlegmator, were manufactured in France. The rest of the equipment was made in the United States. The hot oil is charged to the still with a Dow surge pump. All other pumps on this still were furnished by Union Steam Pump Company. Air for the control instruments is supplied by a Westinghouse steam-driven compressor, similar to those installed on locomotives to supply air for the brakes.

The topping plant was designed by M. W. Kellogg Company to process 6500 barrels of crude per day. The still is complete, with all the latest improvements in the form of automatic controls, exchangers, both liquid and vapor, strippers for light and heavy gas oil, kerosene and heavy naphtha. The 375° F. end point straight run gasoline is taken from the top of the 90-foot tower. The charge and reflux pumps are Pacific type, driven by Terry steam turbines, and controlled by Fisher pressure regulators. The steam to the unit is controlled by an air-actuated Fisher steam regulator. This regulator reduces the steam pressure from 180 to 150 pounds, and makes a perfect line on the chart.

The 3000-barrel rerun still was designed by Southwestern Engineering Corporation. It is of unusual design in two instances: (1) the vapor condensers are enclosed and form part of the vapor line; (2) the fresh feed is charged direct to the bottom of the tower. This method assures a better overhead product, and is easier on tubes, due to the light ends flashing off in the tower and eliminating a lot of vaporizing in the tubes. The pumps furnished for this still are Union Pacific centrifugals driven by vapor-proof electric motors. The automatic controls were furnished by The Brown Instrument Company, and include an automatic fire control for the still.

The stabilizer is of Southwestern design. It operates at 175 pounds pressure, and stabilizes all the Cross and Dubbs production to a vapor pressure of 12 pounds per square inch on the Reid bomb. The non-condensible gas and light products removed by the stabilizer are allowed to expand into a gas holder. A predetermined amount of light ends is condensed for reflux, by regulating the amount of water to the vapor condenser. Operating the unit this way, all danger of freezing up the pressure regulator on the discharge line from the reflux drum is eliminated.

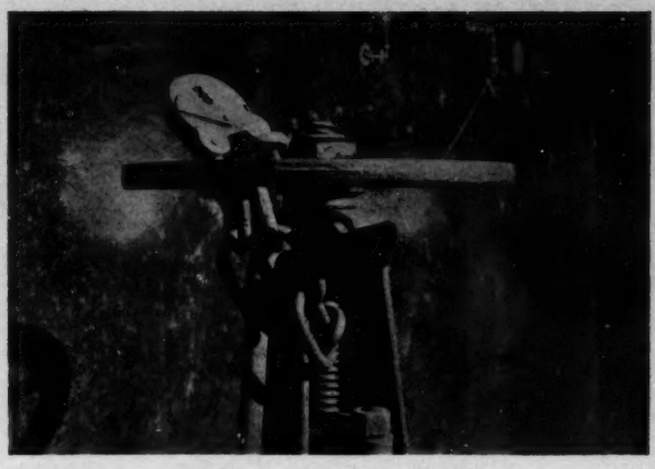
The vapor recovery plant receives the gas from the Cross and Dubbs stills at 20 pounds pressure, and boosts it to 45 pounds through the absorber. The tank vapors are recovered also, and absorbed in another absorber tower. The production from the gas recovery system is blended with the Cross make, and stabilized along with it. The stripped gas is burned under the cracking stills. Any excess is sent to the boiler house.

The Cross runs to 375°F. end point overhead, and after it is stabilized, it is treated in the contrifugal acid treating plant, and finished without rerunning. The Dubbs pressure distillate is rerun after acid treating. The treating plant is of unusual design, and was discussed fully in a recent issue of this magazine. (Ref. & N.G.M. Vol. 11, No. 5, May, 1932, page 312.)

The sweetening plant consists of four settling tanks 7 x 30 feet; two sulphur tanks 2 x 6 feet; and two square caustic melting tanks mounted 12 feet in the air, so that they will drain into the two working tanks. Three of the settling tanks are mounted in a horizontal position; one to settle caustic solution, the other two to settle the doctor solution. The fourth settling tank is mounted in a vertical position, and is packed with rock; starting at the bottom with fairly large rock, and gradually reducing in size until the top layer is fine chat. No water wash is used in the sweetening operation. Any blackstrap carried over is removed by the rock filter. Periodically the filter bed is washed down with water. All pumping equipment was supplied by Union Steam Pump Company. The mixing nozzles are 10-inch Duriron; three for caustic and three for doctor and sulphur. This plant successfully handled as high as 800 barrels per hour.

The boiler house was designed by Roberts Engineering Company. The boilers are of French make. The electric generator is a Moore. The above mentioned units, together with a very complete machine shop, garage, club house, residences for the executives, two loading docks on the river, two artesian wells for boiler feed water, and storage for 500,000 barrels of crude, and about an equal amount of storage for finished products and working tanks, covers the principal items found at this plant.

The various engineering firms sent experienced operators to France to start their equipment, and to instruct the French how to operate. The French were very slow in learning, because the work is foreign to anything they were accustomed to doing. The French worker took little pride in his work. A reason for this might be found in the cloak of protection thrown around him by his government, which is paternalistic and bureaucratic. Forty-eight hours a week is all the employee is allowed to work. Permission to work a



French Government Regulations Require Rigid Inspection, and the Locks Shown on These Valves Are Calculated to Avoid Any Unauthorized Movement of Oil.

man overtime must be obtained from a district labor commission. All men not on shift work must leave the plant for their lunch. It is against the law for them to eat on the plant property. They have sick benefits, paid for by the workers, the employer, and the state. These benefits are for the whole family. If a man's child becomes sick, he draws a small sum each two weeks. Wages paid at this refinery were as follows:

	Cents per hour
Laborers	10 to 12
Clerks	15 to 18
Operators	16 to 20
Stillmen	20 to 24
Firemen	15 to 20
Helpers	15 to 20

The French government stations about 10 customs men at the refinery. The refiner must furnish these men homes, garden spots, and offices. These men lock and seal all tank valves. To pump in or out of a tank, it is necessary to get a customs man to unlock the valve. Customs men gauge all tanks each day at five different gauge holes. All lines must be laid on top of the ground, so they can see where each product goes. The tank farms are surrounded by high fences, and each gate has two locks. The keys are held by the customs men. All automobiles entering the plant must have their gasoline tank gauged by customs men, and again when departing. A large amount of gasoline is barreled at this plant for Africa and customs men require each barrel to be weighed before and after filling. The refiner is not allowed to use an average figure.

These customs men wear a gorgeous uniform of brilliant blue, with a scarlet stripe on the trousers, and a huge cloak. They are very ornamental, but highly detrimental to efficient operation.

This refinery was wholly owned by the French until a few months ago, when The Texas Company bought a large interest in it. (Ref. & N.G.M. Vol. 11, No. 2, Feb. 1932, page 107A.) Since that time, an American manager has been placed in charge, and he has the plant running at full capacity, whereas before it was not unusual to shut down for Sundays and holidays, and every once in a while to have a couple of weeks' vacation. But those days are gone, much to the French working man's disgust.

COMPOSITION AND KNOCK RATING OF *Straight Run* Pennsylvania Gasoline

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WITH the one exception of its knock rating, Pennsylvania straight run gasoline is a quality product. It has the proper volatility so that carburetion and combustion in an engine is satisfactory; it is free from sulfur and other corrosive materials; it is a stable product with no tendency to form gums or deteriorate in storage. However, the recent demand for anti-knock quality has degraded the position of Pennsylvania as well as many other straight run gasolines.

Because straight run gasoline constitutes about 30 per cent of Pennsylvania crude oil, an investigation was started to determine what straight run gasoline really was.

While it is known to consist of hydrocarbons, practically nothing is known concerning the nature of these hydrocarbons, much less, in what amounts they are present in the gasoline. It was hoped that this fundamental information would be of practical importance in devising means for improving its anti-knock quality.

The problem of the composition or analysis of gasoline is really not a new one. For some 50 years various investigators have studied the composition of petroleum and yet very little is known today. After careful study of the various methods of effecting the separation of the numerous substances present, it appeared that fractional distillation was the most promising. Further analysis of the principles of fractionation led to the construction of two fractionating columns, one about 30 feet, the other about 50 feet in height. These columns were found to be effective to the point of separating two hydrocarbons with boiling points as close as 6° F., in one distillation, a degree of refinement in distillation hitherto unknown.

When straight run Pennsylvania gasoline was fractionated in these improved columns, remarkable separations were effected. While no hydrocarbon was obtained pure in this one fractionation, the various constituents were, nevertheless, concentrated many fold over the small proportions in which any one of them existed in the gasoline. So successful were these fractionations that it was possible in one or two further fractionations to obtain materials of a high degree of purity such that their identification was definite and the quantities in which they were present readily determinable.

FRACTIONATION OF 510° F. END POINT GASOLINE

Bradford crude oil from flooded wells was topped by a simple batch distillation to obtain the gasoline. A considerable amount of low boiling material came off the crude at the beginning of the distillation. This was condensed by means of "dry-ice," but these light ends were not investigated since they were known to consist of propane, butane and pentane. The distillation was carried on into the kerosene to insure the removal of all the gasoline from the crude. This distillate, comprising 39 per cent of the crude, is called, for purposes of identification, "510° F. end point gasoline." An Engler distillation of this material shows:

I.B.P.	10%	50%	90%	E.P.
123	185	283	458	510° F.

This material was fractionated in the column three inches in diameter and about 30 feet high, 165 fractions being obtained. Physical tests such as specific gravity, boiling point, and refractive index were made. In addition the knock rating of various fractions was obtained on an Ethyl gasoline knock testing engine. The knock rating is the number of cubic centimeters of lead tetraethyl which must be added to the fraction to equal the old Ethyl gasoline standard of 74 octane number. In some cases the fractions were better than 74 octane number and these tests are rated with a minus (—) sign and indicate the number of cubic centimeters of lead tetraethyl which must be added to the 74 octane number standard to equal the knock rating of the fraction.

The data in Table I characterize the results obtained. It is seen that the knock rating is alternately high and low as the boiling point increases. These results are contrary to previously reported data on the fractionation of gasoline where it was found that the knock rating steadily got worse as the boiling point increased.

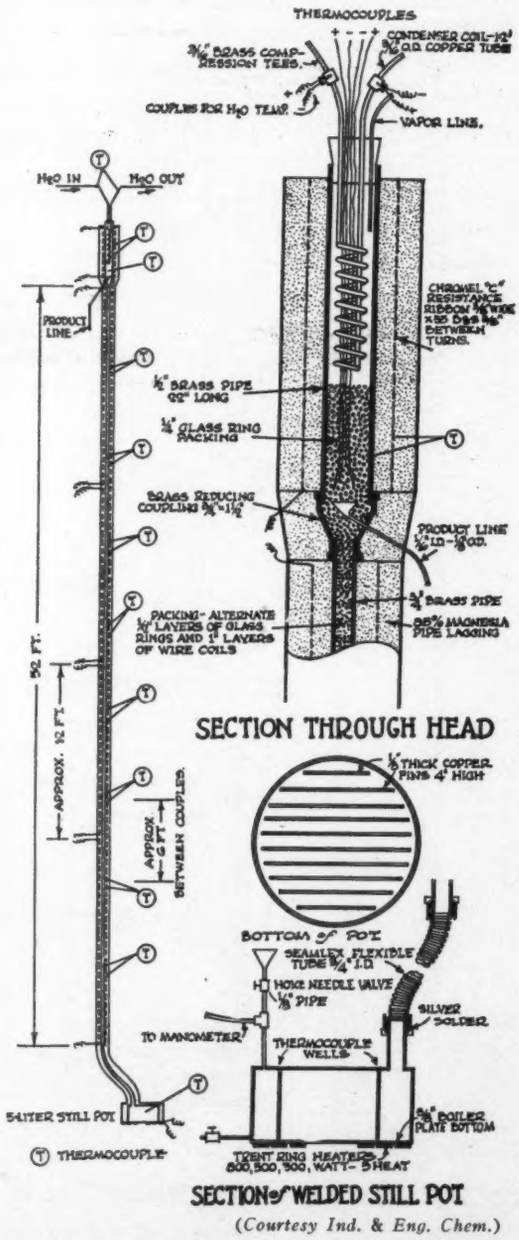
*Presented at the 2nd Pennsylvania Petroleum and Natural Gas Conference, Pennsylvania State College, State College, Penna., May 21, 1932.

TABLE I.
Fractionation of 510° F. End Point Gasoline

Boil. Point °F.	Vol. % Distilled	Refractive Index (20/D)	Specific Gravity (20°C.)	Knock Rating
174	19	1.4055	0.725	0
203	25	1.3958	0.701	6
219	35	1.4307	0.768	0
255	48	1.4070	0.727	16.5
277	54	1.4430	0.786	0
300	61	1.4155	0.742	17
329	68	1.4373	0.780	3.7
343	75	1.4225	0.759	39.0
363	79	1.4350	0.778	16.5
381	83	1.4325	0.773	35
399	85	1.4394	0.785	25

The knock rating is the number of cubic centimeters of lead tetraethyl required to make the fraction equal to 74 octane number (old Ethyl Gasoline Standard).

These data show that the knock rating alternates between very wide limits as the boiling point increases. This is because the column had concentrated effectively the normal paraffin hydrocarbons so that the bad knocking fractions contained them. Such a fraction is then followed by fractions containing branched paraffins, aromatic and naphthenic or cyclic hydrocarbons, all of which possess good anti-knock properties. Then follows a fraction in which the next higher boiling paraffin is concentrated, and a correspondingly bad knock rating appears.



(Courtesy Ind. & Eng. Chem.)

Detail of Column 27 Feet Long, Three Inches in Diameter

FRACTIONATION OF 175-225° F. NAPHTHA

Since there were so many constituents present in the "510° F. end point gasoline," and each in a very small amount, it was interesting to see what separations were obtainable when a narrower boiling material was fractionated. For this purpose a naphtha from Bradford crude with a boiling range of 175 to 225° F. was fractionated. Some of the results are given in Table II. For material with the same boiling point, it is seen that the variation in knock rating is even greater than in the data given in Table I.

The knock rating now varies from —8.7 to +9.0. That is, in one case 8.7 cc. of lead tetraethyl had to be added to the Ethyl standard of 74 octane number to equal this fraction, and in another case 9.0 cc. of lead tetraethyl had to be added to the fraction to equal the Ethyl Standard of 74 octane number. This naphtha cut contains normal heptane, and this is the material largely responsible for the knock. In fact, refractionation of certain fractions yielded normal heptane of about 97 per cent purity. The principal hydrocarbons in this 175-225° F. naphtha in the order of increasing boiling point are normal hexane, benzene, cyclohexane, isomeric branched heptanes, normal heptane, methylcyclohexane, and a very small amount of toluene.

REDISTILLATION OF THE MATERIAL FROM NORMAL HEPTANE THROUGH NORMAL OCTANE (BOILING RANGE 200-260° F.)

The knock ratings given on the previous materials are for each fraction alone. In order to get an idea of the knock rating of these substances or fractions in concentrations approximating their occurrence in the gasoline, the rating was determined for 10 volume per cent blends of several fractions in a base gasoline. This base gasoline was Standard reference fuel B, of 67.5 octane number, supplied by the Standard Oil Company of New Jersey. In Table III are some of the data obtained from 10 per cent blends of fractions from material which had been fractionated twice. The boiling range of this material was 200 to 260° F. The knock rating is the number of cubic centimeters of lead tetraethyl required to bring the Standard reference fuel B, of octane number 74. The Standard fuel B alone requires 0.66 cc. of lead tetraethyl to equal 74 octane number.

Table III shows that the materials boiling at 208 and 257° F. are particularly bad knockers; 10 per cent in the base gasoline of 67.5 octane number lowers its octane number to 60 to 62. (A gasoline requiring 1.5 cc. lead tetraethyl for 74 octane number has an octane

TABLE II.
Fractionation of a 175-225°F. Naphtha

Boil. Point °F.	Vol. % Distilled	Refractive Index (20/D)	Knock Rating
150	5	1.379	
154	10	1.388	
175	18	1.414	—8.7
191	23	1.395	
193	30	1.393	
194	38	1.394	+0.8
205	45	1.393	+8.8
208	56	1.398	+9.0
210	74	1.423	+0.3

The positive sign (+) in the knock rating indicates the number of cubic centimeters of lead tetraethyl required to make the fraction equal to 74 octane number. The negative sign (—) indicates the fraction to be better than 74 octane number and shows the number of cubic centimeters of lead tetraethyl which must be added to 74 octane number fuel to equal the fraction.

TABLE III.
Redistillation of the Heptane—Octane Fraction (Boiling range 200-260° F.)

Boil. Point °F.	Vol % Distilled	Refractive Index (20/D)	Knock Rating	Compounds Present
208	4	1.383	1.5	normal heptane
209	6	1.395	1.2	
210	15	1.418	0.7	methyl cyclohexane
220	25	1.428	0.65	
242	38	1.398	0.0	branched octanes
250	63	1.420	0.0	di methyl cyclohexanes
257	83	1.398	2.0	normal octane

The knock rating is the number of cubic centimeters of lead tetraethyl required to bring Standard reference fuel B, of octane number 67.5, containing 10 per cent of the fraction, to octane number 74.

TABLE IV.

Rapid rise in B. P. between 102-126°F. (39-52°C)	Boil. Point °F.	Boil. Point °C.	% in 400°F. End Point gasoline
2,2-dimethylbutane	122	49.7	absent
2,3 dimethylbutane	137.3	58.5	0.4
2-methylpentane	140.5	60.3	2.2
3-methylpentane	146	63.3	0.65
n-hexane	156.2	69	3.3
Rapid rise in B. P. between 158-171°F. (70-77°C)			
benzene, naphthene and some paraffins 170.6-177.8		77- 81	1.3
Rapid rise in B. P.			
isomeric heptanes 188.6-195.8		87- 91	4.5
n-heptane	209.1	98.4	4.0
methylcyclohexane	213.5	100.8	3.7
Rapid rise in B. P.			
toluene	231.8	111	0.25
dimethylcyclohexanes and isomeric octanes 235.4-246		113-118.8	5.5
Rapid rise in B. P.			
n-octane	257	125	-3.9

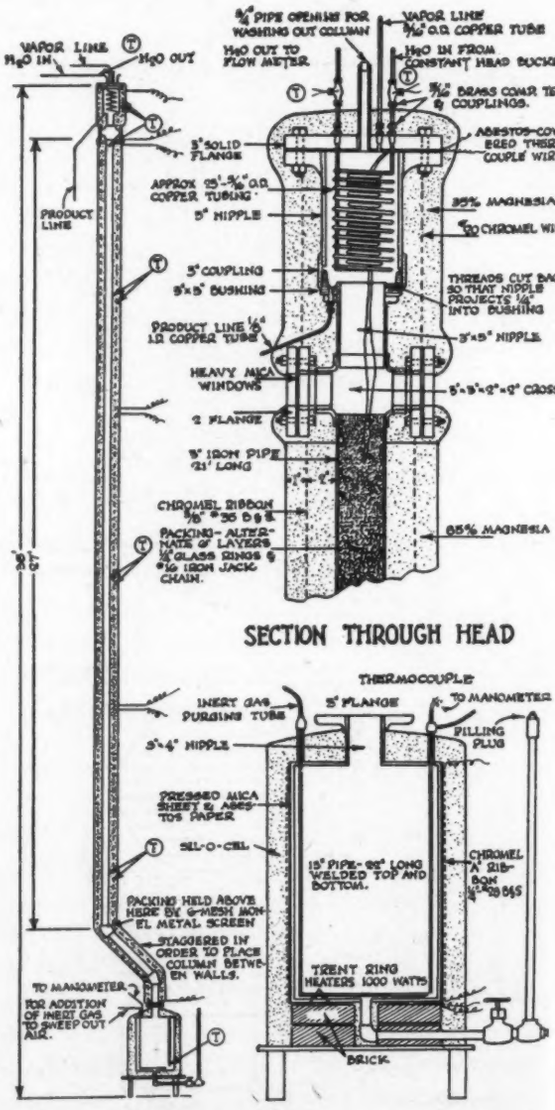
number of about 62, and one requiring 2.0 cc. of lead tetraethyl to equal 74 octane number has about a 60 octane number.) In addition, it is of particular interest to note that the intermediate material, namely, that boiling from 210° F. to above 250° F. is of very satisfactory knock rating, in most cases the fractions actually improving the rating of fuel B. It has been found that the material in the fraction boiling 208 to 209° F. is normal heptane, and that in the 257° F. fraction is normal octane. Both these normal paraffins are known to be bad knockers.

COMPOSITION OF STRAIGHT RUN GASOLINE

Sufficient data have been obtained so that the proportion of the various substances from pentane (boiling point 98° F.) through normal octane (boiling point 257° F.) can be stated with reasonable certainty for the straight run gasoline from Bradford crude. Certain of these substances were isolated in an exceptionally high degree of purity considering that only fractionation was used for the separations, and no chemical means. The data are given in Table IV. Since constant boiling mixtures are reported for certain of the hydrocarbons, it is interesting to note that neither the constant boiling mixture of normal hexane and benzene, nor that of normal heptane and methyl cyclohexane were found.

IMPROVEMENTS IN ANTI-KNOCK QUALITY

While the above data show certain facts regarding the constitution of straight run Pennsylvania gasoline, they hardly indicate the results which may be obtained in concentrating the knocking fractions when using more thorough fractionation. In order to procure this neces-



(Courtesy Ind. & Eng. Chem.)

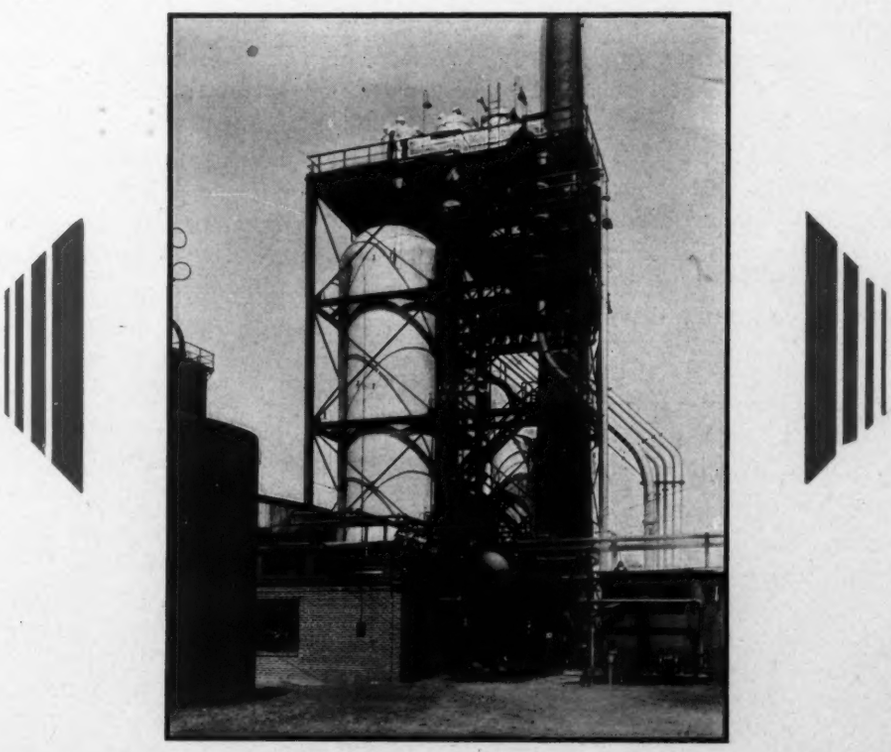
Detail of Column 52 Feet Long, 2/4-inch in Diameter.

sary information the work is being continued on a larger and more efficient scale. These results may then lead to definite conclusions regarding the practicability of effecting the necessary separations in the gasoline. The work to date has led to the following conclusion. The knock in the straight run Pennsylvania gasoline is largely caused by the normal paraffin hydrocarbons despite the fact that there is probably not more than 20 per cent of these present in the gasoline. Any one normal paraffin is present to the extent of two to five per cent.

It is interesting to note the following points. This discussion is not intended to overemphasize the results or be in any way speculative. The average for the knocking normal paraffins in the gasoline is about normal octane. It has been found that when 20 volume per cent of normal octane is added to the Standard fuel B of 67.5 octane number, the octane number is reduced to 50, or if the reverse is considered, if it were possible to withdraw 20 per cent of normal paraffins averaging normal octane, a 50 octane number fuel might be raised to 67.5 octane number. In contrast to the withdrawal of knocking materials, the 50 octane number fuel could be raised to 67.5 octane number by the addition of an anti-knock fuel. However, it would require that about 32 per cent benzene be added to the 50 octane number fuel to obtain 67.5 octane number. Very few cracked gasolines are equal to benzene in blending for the reduction of knock; in this case over 50 per cent of a good anti-knock gasoline such as made by cracking would be needed to raise the 50 octane fuel to 67.5. Of course, the addition of high anti-knock gasoline to low anti-knock gasoline increases the total volume of gasoline available. Aside from the question of the quantity of gasoline available, considering instead its quality, it appears from the above data as well as a variety of other similar data, that greater changes in anti-knock quality can usually be effected by removing the bad knocking constituents rather than by adding to the gasoline the same amount of a high anti-knock blending gasoline.

The question may then arise as to what to do with these knocking fractions if they are removed. First, it is likely that fractions with as narrow a boiling range as these would find application in solvents, or in more direct chemical uses where they would be of greater value than as gasoline. Second, from all the information available, it appears that Diesel engine fuels should be low octane number fuels. These bad knocking fractions while unsuited for a gasoline engine fuel, may be highly desirable for blending to make premium quality Diesel fuels.

While many phases of this work appear, and many interpretations are possible, the primary purpose is to submit these data as essentially fundamental information and as a basis for additional work. The higher boiling fractions of the gasoline deserve particular study, since they contribute largely to the knock. Through the accumulation and study of such data on chemical composition and knock rating, one, at least, of several possibilities may be of practical importance for improving the knock characteristics of straight run Pennsylvania gasoline.



Effect of *Vacuum* on Lubricating Oil Distillation

R. S. DANFORTH, M., A.S.M.E.

THE accompanying discussion of the effect of vacuum on lubricating oil distillation by R. S. Danforth, was presented recently before the San Francisco Section of the American Society of Mechanical Engineers and has seen publication in "Mechanical Engineering," the journal of the society. In this writing the author discusses the effect of temperature upon the composition of vapor, stressing the benefits of low temperature; and compares the operation procedure and costs of dry vacuum and wet of steam vacuum distillation. Suggested designs for fractionators and condensers are presented.

FOR some years, it has been known that the vacuum distillation of lubricating oils possesses many advantages, and the purpose of this paper is to bring out some of its basic features. The benefits of the vacuum process are mainly in the reduction of cracking, in the improved separation of fractions, and the reduction of heat input and condensing requirements.

In lubricating oil distillation, cracked products are usually less desirable. The extent of cracking depends mainly on the temperature and the time of exposure, the heavier molecules cracking at a lower temperature. C. R. Burch reported in Proc. Royal Soc. Vol. A123—1929, experiments on Pennsylvania and other distillates indicating a cracking activity starting at temperatures varying between 584 and 644°F.

In the distillation of a lube oil in a shell still, on account of long exposure, gas evolution usually becomes quite objectionable around 640°F. while in the modern pipe still, the limit of operation from this point of view is above 700°F., dependent on the type of oil.

EFFECT OF TEMPERATURE UPON COMPOSITION OF VAPOR

An important feature in distillation is the effect of a low boiling temperature in greatly decreasing the percentage of heavy fractions in the vapor. By Raoult's law, the ratio by weight of the lighter vapor fraction to the heavier equals the ratio of their weights in the liquid multiplied by the ratio of their vapor pressures. With a lower temperature, the vapor pressure ratio is greatly increased, so that the vapor has much less of the heavier fractions. In the following example, taking merely two fractions for simplicity, the percentage of heavier fraction in the vapor is reduced from 29.2 per cent when distilling at 800°F. under 974 mm. absolute pressure, to 5.1 per cent distilling at 550° and 32 mm. pressure, or to 1.9 per cent at 450° and 5 mm. pressure.

As this increased separation is repeated on each plate of a fractionating column, the amount of reflux in fractionation, the heat required to re-evaporate the reflux and the heat input to the condenser are all reduced with lower temperature operation. The time of exposure and extent of cracking are decreased with the lessened amount of reflux. In distilling the heat required is reduced by the smaller amount of heavier fractions evaporated.

Chart 1 shows the variation of vapor pressure with temperature for normal hydrocarbons of the paraffine series. Mixtures of oils of equivalent boiling points follow practically the same curves.

For example—suppose we are distilling a lubricating fraction of 296 molecular weight from a heavier fraction of 492 molecular weight, the vapor in equilibrium with a residuum containing 10 per cent by weight of the lighter fraction. At a distillation temperature of 800°F. the vapor pressure of the lighter fraction is 5000 mm., the heavier fraction 230 mm. and their ratio 21.7. The ratio of the weight of the lighter fraction in the vapor to the heavier fraction equals $1/9 \times 21.7 = 2.42$. This is equivalent to 70.8 per cent lighter fraction and 29.2 per cent heavier fraction in the vapor. Distilling at 450° the heavier fraction in the vapor will be reduced to only 1.9 per cent instead of 29.2.

By Dalton's law, the total still pressure equals the

sum of the partial pressures of the fractions. The partial pressure of a fraction is equal to its vapor pressure multiplied by its mol fraction in the liquid. (The number of mols equals the weight in pounds divided by the molecular weight). The mol fractions in the above liquid would be 0.16 and 0.84 respectively. The still pressure would be 974 mm. at 800°F. and 5 mm. at 450°F.

The effect of reducing the boiling temperature is shown in the following table:

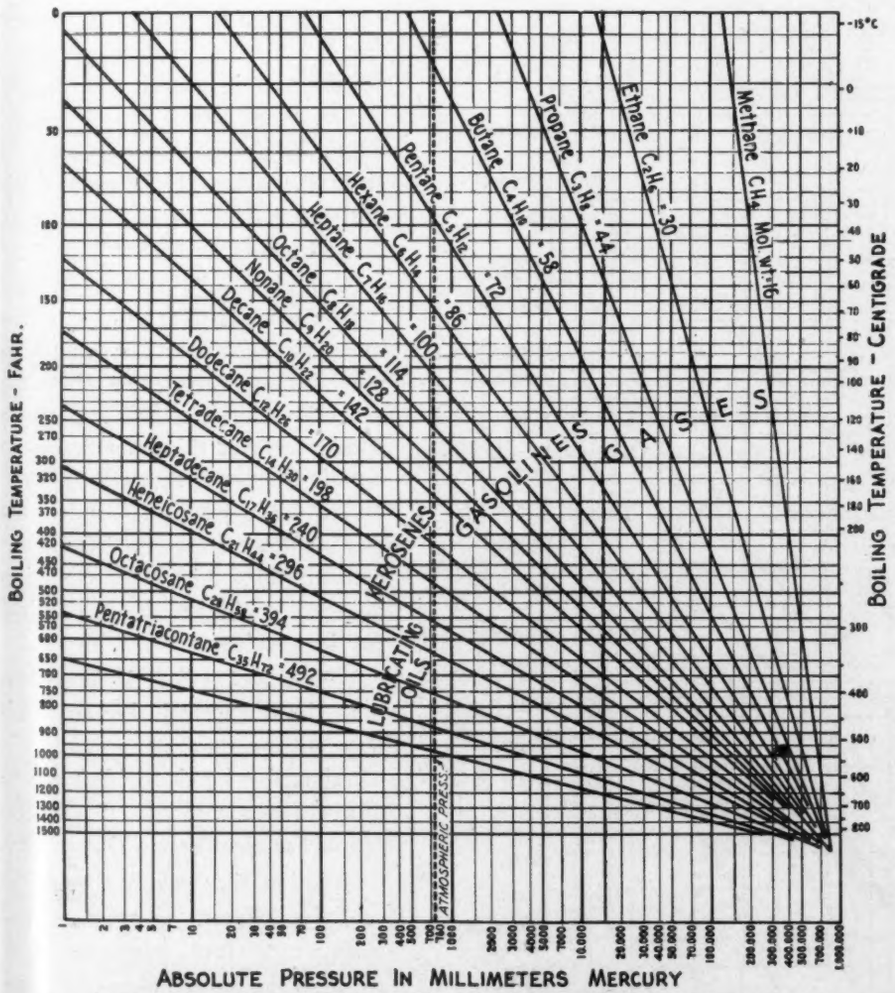
Vapor Composition, Residuum Retaining 10 Per Cent By Weight of Lighter Fraction

(Two fractions having molecular weights of 296 and 492)

Temp. Degr. Fahr.	Vapor Press. Ratio	Ratio Wts. in Vapor	Per Cent Heavier Frac. in Vapor by Wt.	Still Press. Mm. Mercury
800	21.7	2.42	29.2	974
700	43.2	4.80	17.2	281
600	97.8	10.9	8.4	76
550	167.	18.5	5.1	32
500	268.	29.8	3.3	13
450	470.	52.3	1.9	5

At 450°F. the ratio of the lighter fraction in the vapor to the heavier is over twenty times the ratio at 800°F.

VARIATION OF BOILING POINTS WITH PRESSURE



Method of plotting according to E.R.Cox Ind. and Engr. Chem. 1923 p. 592.
Boiling points below 200 mol. wt. from treatise on Distillation by C.V. Rechenberg.
Above 200 mol. wt. from Day "Petroleum Ind" Vol. 1 page 470.

CHART 1.

As a further example of the benefit of low temperature upon relative volatilities assume it is desired to remove a light fraction of 128 molecular weight from a lube-oil fraction of 394 molecular weight. Assuming 0.1 per cent by weight of the light fraction retained in the residuum the results are as follows:

Temp. F.	Still Pressure	% Heavier Fraction in Vapor by Weight
750	808 mm.	93.5
700	424	90.4
600	115	77.
500	30	48.8
400	9	17.4

With high vacuum distillation sufficient separation might be secured in some cases to eliminate the use of fractionators entirely.

DISTILLATION TEMPERATURE

The distillation temperature should therefore be as low as possible in order to improve the separation of fractions, reduce the quantity of gases formed by cracking, secure the highest quality product, and operate with the lowest heat input.

The distillation temperature can be lowered by reducing the pressure by operating under a vacuum, or by indirectly reducing the partial pressure of the oil vapors by the presence of steam.

VACUUM AND STEAM DISTILLATION

In dry vacuum-distillation, the boiling point is lowered solely by reduction of pressure. If the liquid is under a hydrostatic head the low pressure will not be effective, so the main essential is to properly expose the liquid.

In steam distillation, the liquid is exposed at the surface, and in the steam bubbles, to a mixture of oil vapor and steam. The total pressure is divided between the partial pressures of the oil and the steam. The boiling point corresponds to the partial pressure of the oil, and is considerably lower than the boiling point corresponding to the total pressure.

AMOUNT OF STEAM REQUIRED

Assuming that the steam becomes saturated with oil vapors, the injection or distillation steam

required per pound of oil distilled to secure a given boiling point is given by the following formula:

$$a = \frac{18\ (P-p)}{Mp}$$

Where a = the lbs. of injection steam per pound of oil distilled over
P = the total absolute pressure in the still
p = the partial pressure of the oil corresponding to the desired boiling point (in same units as P)
M = the average molecular weight of the vaporized oil.

With steam distillation in shell stills, owing to the high velocity, large volume and slow diffusion, it is difficult to secure a uniform saturation of the steam with oil vapors and between two and three times as much steam as theoretically necessary is often used. With pipe stills where the steam is brought into more intimate contact between one and one and a quarter times the theoretical amount is used. Chart 2 shows the injection steam required for steam distillation in accordance with the above and also the yearly cost per thousand barrels distilled over per day. The steam should be super-heated above the distillation temperature otherwise it will absorb heat from the oil being distilled. The cost of condensing water is not included.

Considering simple distillation only, without reference to fractionating towers, in one dry vacuum plant the air leakage and non-condensable gases were less than 22 cubic feet of free gas per minute for 3000 barrels per day oil distilled. To handle this volume of gas at 5 mm. absolute pressure will require, with one type of vacuum pump, approximately 62 operating horsepower and at 1½ cents per kilowatt hour, some $6075 per year. To secure the same boiling point by use of live process steam in pipe stills at 50 mm. pressure (28-inch vacuum) would require a process steam supply costing some $60,000 or $70,000 per year with steam at 35 cents per 1000 pounds, without considering the cost of cooling water required for its condensation or the operation of the vacuum apparatus. If low cost steam is available, such as the exhaust from steam pumps, this cost will be greatly reduced or possibly even eliminated.

If no process steam is used a high dry vacuum can be effectively maintained as only the noncondensable gases, air leakage, and dissolved water vapor have to be handled. If any process steam is used the obtainable vacuum is limited by the cooling water temperature in the steam condenser and is usually around 28 inches. With cooling water around 60°F. 28½-inch vacuum can be secured. With refrigerated cooling water an absolute pressure of 20 mm. could be secured.

A higher distillation vacuum can be secured with process steam by using a booster ejector (Kramer Pat. No. 1,619,348) between the oil condenser and the steam condenser, but this booster has to handle the process steam as vapor under high vacuum besides the gases and air leakage. The steam consumption is therefore considerable and cooling water is required for its condensation.

Where steam cost is important it is therefore desirable to eliminate all process steam and this could easily be done if fractionating towers were not usually required for clean separation of cuts.

Fractionating towers are usually used in commercial practice, and owing to the pressure drop through the bubble plates, it is impossible to secure the full advantage of dry high vacuum distilla-

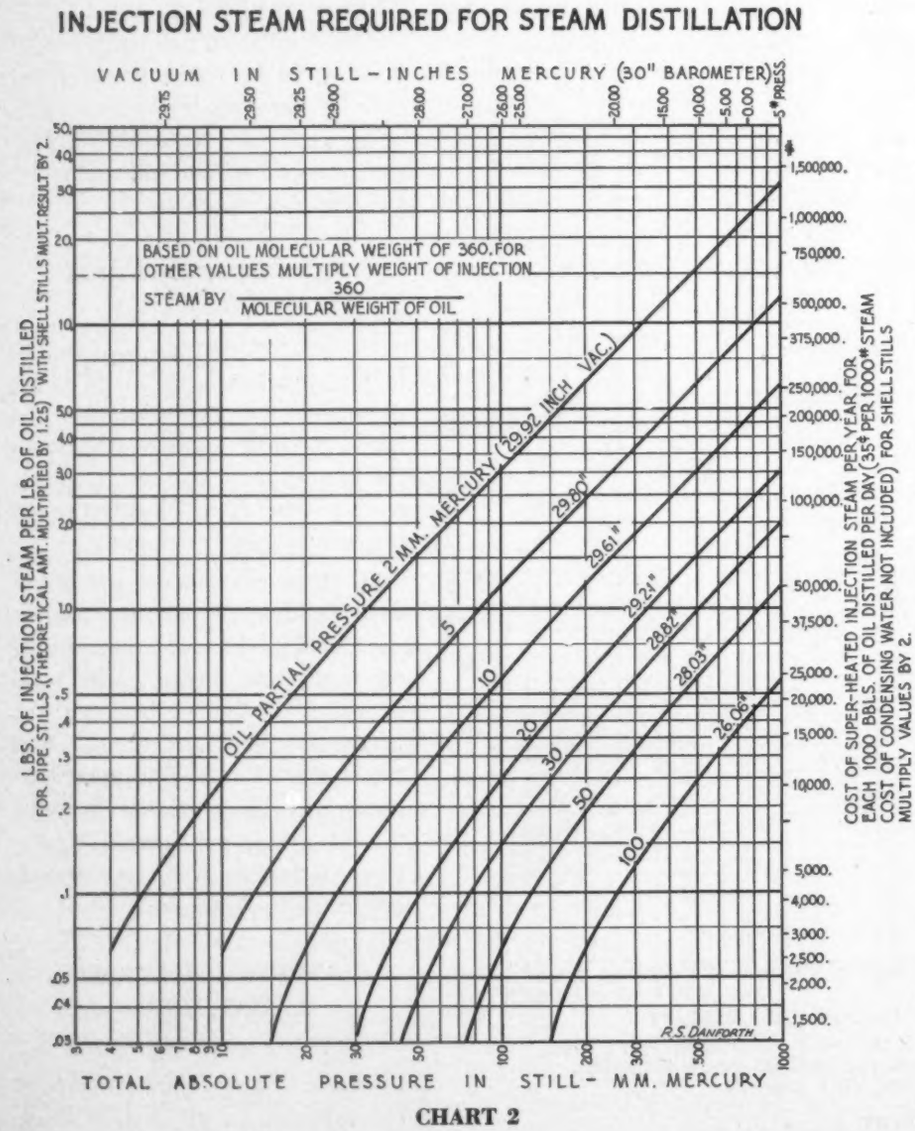
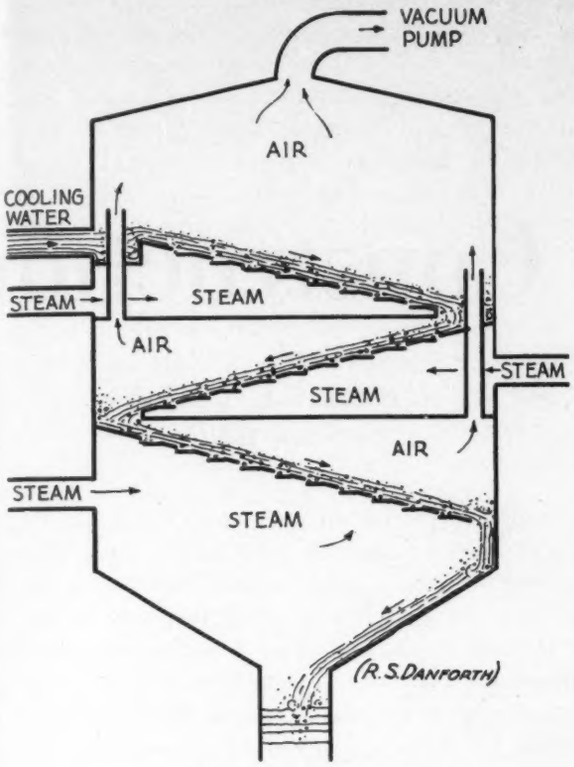


CHART 2



CONDENSER

FIGURE 4

tion. Process steam is therefore customarily used, carrying as high a vacuum as permitted by the condenser cooling water temperature. Various types of fractionating towers, designed for a low vapor pressure drop, have been used, but for various reasons they have not been extensively adopted.

Injection steam in side stream stripping sections was formerly supposed to have a mysterious action in removing the light cracked products. The effect of steam vapor at any point is to lower the partial pressure and boiling point of the oil, but it apparently does not affect otherwise the composition of the vapor. When the boiling temperature is lowered the ratio of the vapor pressures is increased, increasing the percentage of light fractions in the vapor.

If process steam was not needed in the fractionating tower, the lowering of the boiling point required to vaporize in the strippers could be secured by the use of steam and a booster ejector to a separate condenser or by carrying a higher vacuum on the strippers. The volume of fixed gases to be handled would be small.

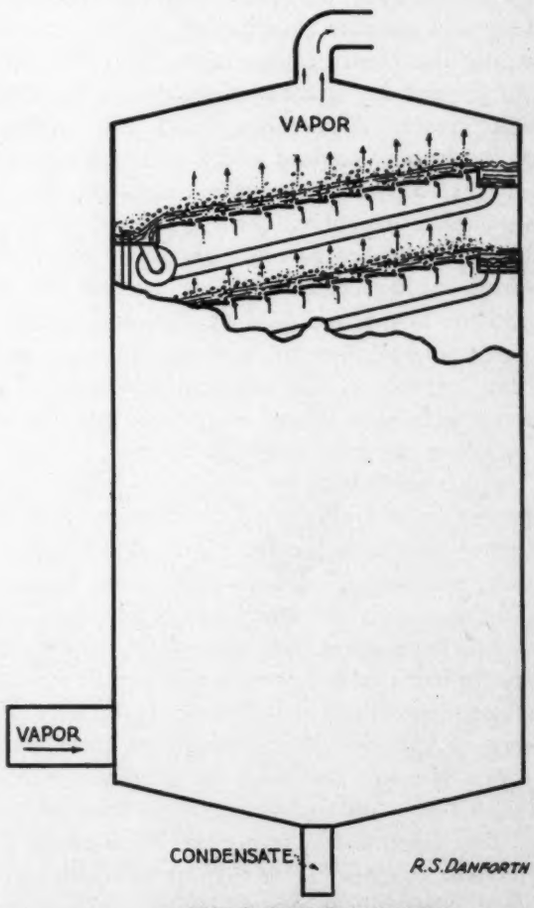
A POSSIBLE FRACTIONATOR DESIGN

As an additional possibility as yet untested, the writer mentions a fractionator in which the plates are inclined and fitted with vapor slots as shown in Figure 3. The liquid on each plate is circulated by pumps, so that it flows over the slots between guiding partitions. The hydrostatic head slightly assists the flow of vapor instead of opposing it, and the pressure losses caused by passing through the usual bubble caps should be greatly reduced.

The tendency to by-pass should be reduced as each bubble of vapor is introduced into a fresh surface of the liquid. The liquid is thoroughly agitated keeping its concentration uniform. The difficulty found in maintaining the plates of the usual bubble towers horizontal would not be present. Entrainment should be materially reduced owing to the vapor leaving the liquid while traveling down the plates, and therefore having a considerable horizontal velocity. A serious objection is the installation of a pump for each plate operating under vacuum at a high temperature and the consequent mechanical difficulties.

SUGGESTED CONDENSER DESIGN

The above principle might also be applied in the design of barometric condensers, securing a quick intermixture of cooling water and vapor, eliminating by-passing, and reducing the pressure drop through the apparatus. Figure 4 indicates one arrangement, circulating pumps for each plate not being required.



FRACTIONATOR

FIGURE 3

Small Cars . . .

START BIG

Refinery Construction

GEORGE REID
Associate Editor

THE principal contributing factor causing the wide spread construction activity in the refining can be traced back to the economic factors affecting the automotive industry. In their efforts to secure sales the automotive industry is concentrating upon the production of light cars, in as much as the small car field represents 85 per cent of that industry's sales. To secure satisfactory performance, the light car must be powered with motors of high compression ratio. This, interpreted in terms that effect the petroleum industry means that gasoline of higher octane ratings (higher anti-knock characteristics) must be produced, and that means more cracking or naphtha reforming units, which in turn, brings about the installation of additional vapor recovery and gasoline stabilization plants.

Lacking the higher compression ratios the performance of present day small cars might have been secured through greater displacement—and this means that larger and heavier engines would be required, which in turn means heavier parts, more weight, in the rest of the automobile assembly. Such a method of approach is all right in so far as the high priced automobile is concerned. However, with 85 per cent of the market being in the low priced field (which, incidentally is to be entered soon by three more motor car manufacturers, according to reports), the automotive industry is vitally concerned with high compression ratios and low weight cars to sell in the $500 to $1000 range.

It is not possible with low weight small cars to secure the greater horsepower, rapid acceleration, high speed, and other desirable features of performance and economy, without high compression ratios. In securing performances with the small car better than that of larger and more expensive cars of five years ago the automotive industry has created a demand for premium motor fuels—gasolines of higher octane number. Ninety per cent of cars for 1932 distribution have compression ratios of 5 to 1 and over. Five years ago this percentage was 21. Automotive engineers have pretty well agreed that compression ratios can reach above 7 to 1 with modern engines before serious difficulties are encountered. Certainly this trend indicates a further raising of octane rating of motor fuels, and therefore the intensive application of the cracking unit in the future.

While conditions in one industry, as outlined above, force the adaptation of new methods in another industry (such as naphtha reforming), some times the "unusual" occurs, as it has in this instance, and the production of increased quantities of finished product, does not indicate an early revival of continuous increases in demand for raw material—in this instance, crude oil. Through the wider application of the cracking and reforming processes now available, the refining industry can materially increase its annual yield of motor fuels, without processing increasing amounts of crude—and this condition contributes much to the lower crude oil demand as forecast by the industry's economists.

The problem of providing motor fuels satisfactory to the modern motor car, and those of the future has brought about much construction activity in practically every refining district in this country and Canada (where import duties have also contributed to construction of new refineries). Likewise many refineries operating old equipment have been modernizing their plants through the erection of new facilities to be enabled to produce closely fractionated motor fuels of higher volatility. Most of the new plants going into service recently are equipped with cracking facilities, or contemplate their early addition.

SOUTHERN STATES

During 1932 and in the Southern states, Coastal Petroleum Company completed construction of a new refinery at Mobile, Alabama, Shell Petroleum Corporation, at Houston, is installing new cracking equipment and vapor recovery and stabilization facilities, while Magnolia Petroleum Company has but recently completed modernization and construction of cracking facilities at Beaumont and Fort Worth, Texas. Bobrose Oil & Refineries, Inc., at Luling, after revamping its recently purchased plant, plans construction of a cracking unit. Valley Refining Company has erected a small plant at McAllen, Texas, and newspaper reports state that a cracking unit will be erected.

Not closely related to the discussion, but indicative of activity in the manufacturing branch of the industry in

the South, is the erection of gasoline plants this year in the East Texas field, where Humble Oil & Refining Company has completed its second plant, Arkansas Fuel Oil Company, operating under the name of Harmony Gasoline Company, has completed a plant near Longview; East Texas Natural Gasoline Company and Trapshooter Reilly Oil & Royalty Company, and Gulf Production Company are building plants, and Hirt & MacDermott, Inc., propose erecting a gasoline plant soon. Other plants in this field were completed last year.

NORTHERN STATES

In the Northern states, Standard Oil Company of Ohio completed modernization of the Solar Refining Company plant at Lima, Ohio; Bartles-Maguire Oil Company at East Chicago, completed erection of a new cracking installation, Standard Oil Company (Indiana) is building the world's largest cracking unit at Whiting (20,000 barrels rated capacity) which takes crude oil direct as the charge. The company plans installation of smaller units of similar type at its Casper, Wyoming, Wood River, Illinois, and Sugar Creek, Missouri, refineries. Louisville Refining Company at Louisville, Kentucky, installed a new recovery and stabilization system, and Indian Refining Company (The Texas Company) erected two additional modern cracking units at Lawrenceville, Illinois. Recently The Pure Oil Company started construction of a new 5000-barrel refinery at Midland, Michigan. White Star Refining Company has started erection of a new type cracking unit of company design at Wood River, Illinois.

EASTERN SECTION

In the Eastern section Gulf Refining Company completed construction of large naphtha reforming units at three of its Eastern refineries, and added coking facilities at the Toledo, Ohio, plant. Atlantic Refining Company completed installing a battery of 12 coking units of Knowles type at Philadelphia. At Baltimore, Continental Oil Company completed installation of a new continuous centrifugal acid treating system. In Pennsylvania, Sherwood Refining Company took over the Mutual Refining Company plant at Warren, Pennsylvania, modernized it, and resumed operations with new facilities for medicinal oil and lubricating oil production at Oil City, The Pennzoil Company is erecting a new type of Dubbs cracking unit. Tidewater Oil Company completed erection of new cracking facilities of large capacity at Bayonne, New Jersey, early in the year.

WESTERN STATES

In the Western states, Midland Oil Refining Company recently completed a new refinery at Denver, Colorado, Jenson Oil Refining Company, enlarged capacity of its Ogden, Utah, refinery and proposed erection of cracking facilities, while at Salt Lake City, Utah Oil Refining Company started modernization of cracking facilities and erection of complete vapor recovery and stabilization equipment. In California, considerable activity has been under way, beginning with completion of Associated Oil Company's new 10,000-barrel cracking unit at Avon, followed by announcement of a new vapor recovery and stabilization system, and still later by reports of contract let for a new vacuum distillation unit. Mohawk Petroleum Company is reported to have let contract for a new refinery at Fruitvale, California; Southern Gasoline Company erected the state's only new gasoline plant this year near the highway between Ventura and Santa Barbara, and Terra Bella Refining Company after the second attempt completed construction of its Terra Bella refining plant. Hancock Oil Company, at its Long Beach plant, erected additional distillation equipment. General Petroleum Corporation, not previously being engaged in cracking on the West Coast has confirmed reports that it will build a 6000-barrel cracking installation at Torrance.

MID-CONTINENT ACTIVITIES

Much activity has been under way or is planned in the Mid-Continent refining area, especially in Oklahoma. Empire Oil & Refining Company at Ponca City, has installed some new reforming (cracking) equipment, Garber Refineries, Inc., at Garber, completed a new reforming unit, added to its recovery and stabilization system and installed new continuous treating equipment, also Rock Island Refining Company at Duncan, completed a new unit for gasoline recovery and stabilization. Champlin Refining Company, at Enid, installed new vapor recovery and stabilization facilities. Sinclair Refining Company officials in Tulsa recently stated that modernization programs would be undertaken soon affecting the Sand Springs plant, and the Coffeyville, Kansas, refinery. Peppers Gasoline Company has erected a new plant for handling Oklahoma City gas.

In Kansas Vickers Petroleum Company has erected a new refinery at Raymond; Skelly Oil Company added asphalt-vacuum equipment; El Dorado Refining Company, El Dorado, added vapor recovery and stabilization equipment, as did National Refining Company at Coffeyville. Standard Oil Company (Kansas) modernized and improved its cracking department and added recovery and stabilization systems, and Phillips Petroleum Company at the Independent Oil & Gas Company plant, Kansas City, has announced that it will erect new and modern distillation facilities (with reports stating that the same company will improve facilities at its Okmulgee, Oklahoma, and Borger, Texas, plants).

In Texas, Marathon Oil Company, Fort Worth, is preparing for installation of new cracking equipment, and other facilities, with plans also affecting the Bristow, Oklahoma, refinery. Oriental Oil Company, at Dallas, has installed cracking equipment of its own design, as has East Texas Refining Company at Longview. Operation of the Pampa and Longview refineries of

Petroleum Refractionation Company, has been taken over by the Danciger interests, with plans calling for cracking equipment at the Pampa plant. Continental Oil Company at its Wichita Falls plant has completed erection of a new vapor recovery and stabilization system.

CANADIAN ACTIVITIES

The protection given refining operations by the Canadian government through the imposition of import duties and anti-dumping laws placed refining operations on a more favorable basis and at the same time made necessary the erection of new plants in Canada by companies marketing in that country.

Construction has been more pronounced during the first half of 1932 than was the case in 1931, during which year the largest installation consisted of a new refinery at East Montreal by British-American Oil Company. Recently, Shell Company of Canada announced plans for a new refinery with cracking equipment at East Montreal, Quebec, and is also building a new refinery and distributing plant at Van Couver, British Columbia. In this same province, Seaboard Oil & Refining Company is building a refinery at North Van Couver.

A second new refinery at East Montreal has been announced by Joseph Elie, Ltd., and the new plant will operate as La Salle Petroleum Refinery, Ltd. Cities Service Company has announced a new Canadian refinery (equipped with cracking facilities) to be erected at Toronto, Ontario. H. C. and R. E. Karels plan a small plant at Regina, Saskatchewan, and in the same province Hi-Way Refineries, Ltd., will build a small refinery at Saskatoon, with plans for other small refineries at points not yet determined. Simrall Refining Company of Canada has completed its plant at Amherstburg, Ontario, and Sterling Oil Refineries, Inc., has likewise completed its refinery at Moose Jaw, Saskatchewan. Northwest Stellerene Company, at Coutts, Alberta, has finished erection of a new Dubbs cracking unit, and Maple Leaf Petroleum, Ltd., also at Coutts, announced plans for enlarging capacity and possibly adding cracking facilities.

Continued expansion of the refining industry in Canada, along with its import duty, is rapidly removing this country from the list of export markets for oil refined in the United States, and it appears that continued exploration and exploitation of the Canadian fields, will ultimately make it unnecessary for many Canadian refineries to import crude.

The foregoing listing does not include all of the activity of construction and expansion in the refining industry for the first six months of 1932 for the reason that all companies do not release such information. A number of companies are known to have installed cracking equipment of their own design concerning which no published reports have been permitted. In addition to the erection of cracking facilities, new refineries, gasoline recovery and stabilization systems, throughout practically all of the eight refining districts, a number of refineries have enlarged steam generating plants, or modernized them; some construction work has been under way in lubricating oil manufacturing departments; cooling water circulation systems have been expanded, waste water recovery, and caustic soda and acid recovery plants have been installed and a number of refineries have improved their fractionation facilities through installation of fractionating columns of modern design.

It appears that as customary, the industry is getting its manufacturing facilities in good order for operation during the winter months, during which time, as usual, it is expected that expansion and construction activities will be reduced to that necessary for efficient operation, consisting mostly of general repairs and maintenance. During the first six months of 1932 a total of 45 major installations have been reported, in the United States, and probably as many more programs of construction have been engaged in concerning which no information has been available.

USE *of* LIME *in the* Petroleum Refinery

SIDNEY P. ARMSBY
Chemical Engineer

PART 3

THIS constitutes part three of the series of articles by Sidney P. Armsby, Chemical Engineer, dealing with the subject of lime utilization in the refinery industry. In the first article the discussion centered around the selection of the right grades of lime for various process operations. The second article explained some of the fundamental principles to be observed in selection of the proper equipment for handling lime.

This article outlines the uses of lime as applied to refining operations and is intended to illustrate, rather than to catalogue, such uses. Prevention of corrosion in tubes, towers, condensers in distillation work is discussed along with similar work covering the cracking plant. Chemical treatment, neutralization, gas scrubbing and grease manufacture are some of the other applications, as are water softening, construction work, sanitation, and neutralization of acid sludges.

ONE of the chief advantages of lime as a chemical reagent lies in the fact that it can be handled so easily, conveniently and safely. Being non-corrosive, it has no harmful action on equipment with which it is handled. If spilled on the ground it causes no trouble, and it can be handled by unskilled laborers without danger to themselves or to others.

The fire hazard is very small with lime. It is possible to start a fire by allowing water to act on quicklime in a confined space and in contact with inflammable material (for example by allowing an ordinary wooden barrel of lime to stand in a few inches of water, or to be rained on). There is little likelihood, however, of such conditions being permitted to exist in any oil refinery. Therefore, the chance of a fire being caused by the slaking of quicklime is very remote, and there is absolutely no fire-risk whatever with any brand of hydrated lime that has been properly hydrated in manufacture.

LOW IN COST

Another worthwhile benefit resulting from the use of lime as a chemical reagent lies in the fact that it is low in cost when compared to other active bases. From an operating viewpoint this is extremely important because of the savings in operation costs which are made possible by the use of this reagent. In those rare cases where handling costs are higher for lime than for other chemicals, it should be borne in mind that the saving in the cost of the lime will usually more than pay such extra handling costs.

HIGH IN EFFICIENCY

The reaction efficiency of lime is high because of low molecular weight and the fact that it can be obtained with a high degree of purity, or "availability." The relative combining weights of calcium oxide, calcium hydroxide and sodium hydroxide may be shown by listing the molecular weights of the quantity of each one required to neutralize one molecule of sulphuric acid, as follows:

Compound	Formula	Molecular weight
Calcium oxide	CaO	56
Calcium hydroxide	$Ca(OH)_2$	74
Sodium hydroxide	2NaOH	80
Sulphuric acid	H_2SO_4	98

This tabulation shows that for neutralizing 98 pounds of pure sulphuric acid there will be required 56 pounds, 74 pounds and 80 pounds, respectively, of the three bases shown. Since none of the three are purchased 100 per cent pure for ordinary process work, let us assume, for purposes of comparison only, that we secure caustic soda of 97 per cent purity; hydrated lime containing 90 per cent available calcium hydroxide, and quicklime with 90 per cent available calcium oxide. Then our tabulation becomes:

Material	Factor		Combining weight pounds
Quicklime	56 x (100 ÷ 90)	=	62.2
Hydrated lime	74 x (100 ÷ 90)	=	82.2
Caustic soda	80 x (100 ÷ 97)	=	82.5
Sulphuric acid	98 x 1	=	98.0

On the basis of such respective purities we see that, for reactions involving combinations with acids, hydrated lime is equally efficient as caustic soda, while only three-fourths as much quicklime is required.

Calcium is a strong base and its salts (both soluble and insoluble) are easily handled under a majority of the conditions existing during the process operations involved in the manufacture and refining of petroleum products.

THE FLOW CHART

In listing or studying the most important applica-

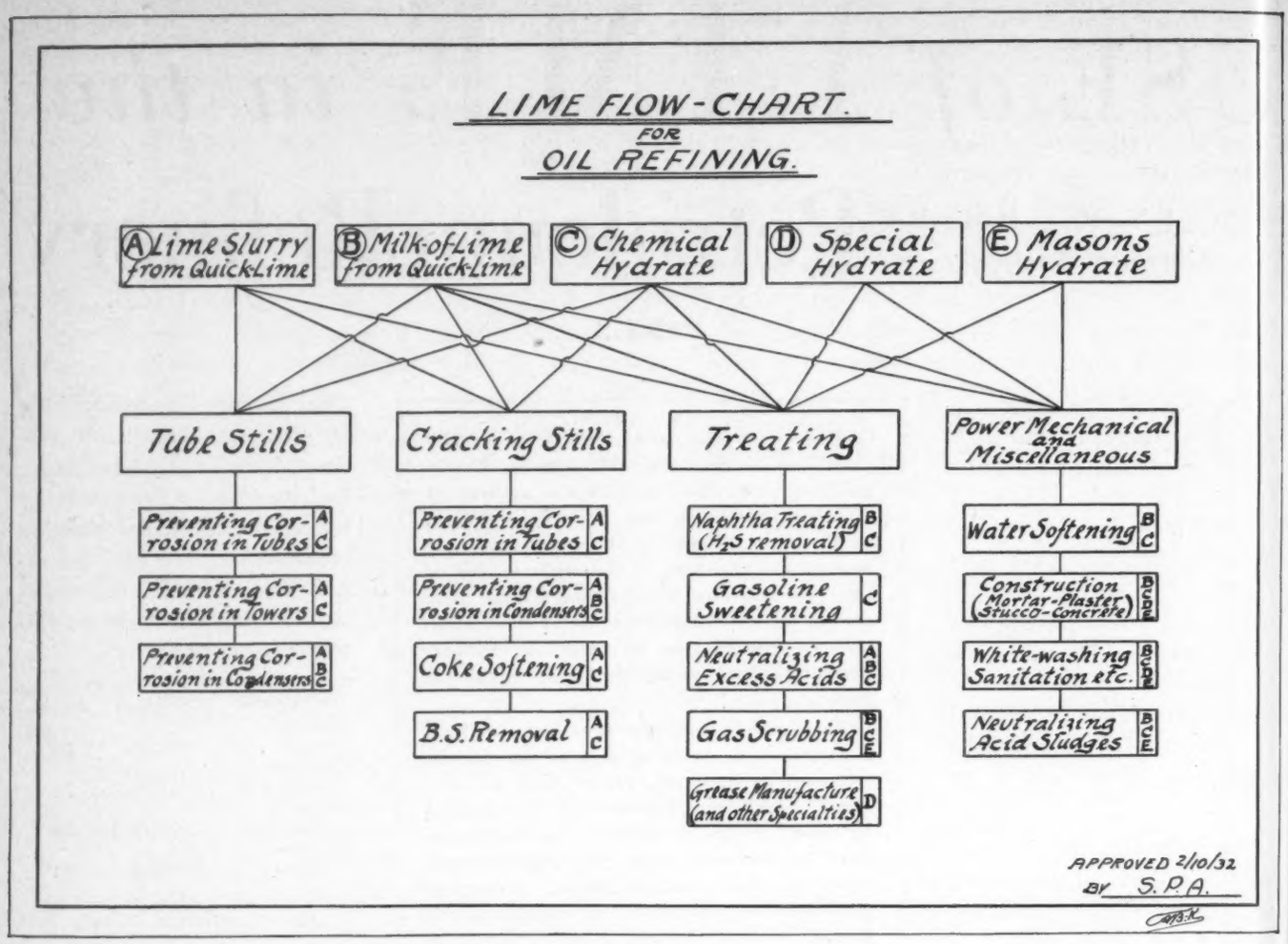

LIME FLOW-CHART.
FOR
OIL REFINING.
A Lime Slurry from Quick-Lime
B Milk-of-Lime from Quick-Lime
C Chemical Hydrate
D Special Hydrate
E Masons Hydrate
Tube Stills
Cracking Stills
Treating
Power Mechanical and Miscellaneous
Preventing Corrosion in Tubes A C
Preventing Corrosion in Towers A C
Preventing Corrosion in Condensers A B C
Preventing Corrosion in Tubes A C
Preventing Corrosion in Condensers A B C
Coke Softening A C
B.S. Removal A C
Naphtha Treating (H2S removal) B C
Gasoline Sweetening C
Neutralizing Excess Acids A B C
Gas Scrubbing B C E
Grease Manufacture (and other Specialties) D
Water Softening B C
Construction (Mortar-Plaster) (Stucco-Concrete) B C D E
White-washing Sanitation etc. B C D E
Neutralizing Acid Sludges B C E
APPROVED 2/10/32
BY S.P.A.

FIGURE 8

tions of lime to refinery practice, the accompanying flow chart (Figure 8) will be found useful as a reference. It is called a "flow chart" because it combines the features of a flow-sheet and a chart—showing first, the possible movements of five different forms of lime reagent to sixteen different operations under four main process groupings and, secondly, showing at a glance which ones of the five reagents are best adapted to any given operation.

Lines leading from the five blocks A.B.C.D. & E, show to which of the four main process groups each form of lime may be applied. Reference letters at the right of each individual operation block show which ones of the five lime reagents are applicable to that particular operation. For example, all five reagents may be used in "Treating" processes but, as shown by the reference letters, only one of them is recommended for gasoline sweetening and a different one for grease making, while three are suitable for gas scrubbing.

GROUP I—TUBE STILLS

*Preventing Corrosion in Tubes**

The necessity of doing everything possible to prevent corrosion in still tubes hardly needs any emphasis here. Every refiner knows the ever-present dangers to life and property that must be guarded against when only a single thickness of metal separates hot oil from live flames.

THE SCOPE OF THE PROBLEM

Research and experimentation are continually being applied to the general problem of corrosion in order to determine causes, effects and remedies and, as more data become available, the cost of corrosion to the refining industry will no doubt be considerably reduced. Developments indicate that one of the principal offenders is the element sulphur, acting in different combinations, such as hydrogen sulphide, various alkyl sulphides and probably also in diverse organic acid combinations which may be formed or dissociated at different temperatures. Some oils of low sulphur content and practically free from hydrogen sulphide are more corrosive than others high in sulphur, thus supporting the opinion that hydrogen sulphide is not the only sulphur compound which causes corrosion of distillation equipment.

Another important source of corrosion may be found in the chlorides which accompany many crude oils and which, under certain conditions, may give

rise to the formation of hydrochloric acid within the distillation equipment.

Among the remedies that have been suggested and tried are; the use of corrosion resistant alloys for still tubes, and chemical treatments of various kinds. Each has its place, and the results obtained vary according to the severity and precise nature of the individual corrosion problem and the suitability of the particular alloy or chemical for the case in hand.

THE LIME TREATMENT

It is worthy of more than passing note that in a majority of cases where lime has been used to treat charging stock the corrosion of still tubes has been greatly reduced, if not entirely stopped. This is probably due in part to the fact that lime, in addition to having a strong chemical affinity for the acids of both sulphur and chlorine, is of itself a preventive of electrolytic corrosion, tending to establish a protective, or passive, coating between the surface of the metal and the hot oil. This theory is subject to argument, but the fact remains that the use of from 0.4 to 1 pound of hydrated lime per barrel of charging stock has been found to be remarkably effective in preventing corrosion in tubes, as well as other parts of distillation units. The exact amount of lime to be used depends upon the character of the oil being charged, and can only be accurately determined by actual trial, supplemented by laboratory analyses and tests. Unlike some chemical treatments, it is perfectly safe to start with an over-dose of lime and work down to the minimum necessary dosage.

Any excess lime present during a test run will not cause caustic embrittlement nor have any other harmful action on the equipment, and the worst that can happen will be an excess of lime carried over into the fuel oil, thereby increasing its ash content. Once the correct dosage has been established, this difficulty is automatically overcome and the process proceeds smoothly. In the meantime, the full benefit of the lime has been secured in all test runs.

The simplest way to apply lime to this operation is to make it into a slurry with a portion of the charging stock and inject this slurry into the main stream entering the still. Methods of preparing and handling such mixtures, from either hydrated lime or quicklime, have already been outlined, and they are shown as alternates on the flow chart.

Chemical hydrate is selected as being more suitable than masons hydrate because of its higher available lime content and greater degree of fineness—equivalent to greater neutralizing power and more complete dispersion. The use of the special hydrate would probably not be justified, because any impurities present are pretty certain to be inert so far as chemical effects are concerned and also because the extra cost is likely to be out of proportion to the value of the increased fineness or available lime content for this particular application. Slurry from quicklime is recommended because the impurities are unlikely to cause any harmful action, and also because the lower cost of such a slurry is almost certain to more than offset any lowered efficiency due to the presence of larger amounts of such impurities.

PREVENTING CORROSION IN TOWERS

If the stock inside the still has been properly treated, so as to neutralize all corrosive action it might have, there will be no need of further treatment in the fractionating towers. Thus, by properly liming the charging stock as it enters the still, we prevent corrosion of towers as well. Consequently, this operation is practically identical with the preceding one and the same considerations govern the choice of lime reagent to be used.

PREVENTING CORROSION IN CONDENSERS

While the corrosion problem in condenser worms may usually be reached via stills and fractionating towers, there may be cases where special conditions will make it advisable to employ separate corrosion prevention methods at this point. This may be done by introducing a small spray or shower of milk of lime so that the distillation products are forced to pass through the lime as they enter the condenser, the excess milk of lime being trapped and recirculated.

Thus we have two optional methods of dosing lime here; through the still and tower as lime slurry, or directly as milk-of-lime. The chemical hydrate (block C) can be used to prepare either of these reagents.

GROUP II—CRACKING STILLS

Preventing Corrosion in Tubes and Condensers

The same factors as cited above for combatting corrosion in tube-still equipment will also govern the choice of liming material to be used in tubes and condensers of cracking units, and the same reference letters covering these operations will be noted on the flow chart—the lime-oil slurry being added to the charging stock as it enters the still.

In this connection, it is of interest to note the experience of The Pure Oil Company at its Smith's Bluff refinery, as reported by R. J. Lawrence. (See The Refiner for August, 1930). We quote from this report as follows:

> "On the cracking stills this rapid corrosion soon gave rise to failure in tubes, return bends, headers and transfer lines. Fortunately no one was injured in any of these failures. Immediately steps were taken toward the elimination of this high rate of corrosion. Careful consideration was given to several methods of reducing the corrosion rate and it was finally decided to employ hydrated lime. The lime treatment was chosen because sufficient amounts of the alkali could be fed into the stills with the charging stock to greatly re-

tard the corrosion, and still not be detrimental to the stills or the products secured. . . . "

"The control of the quantity of lime used and the corrosion rate is handled by the laboratory. Three numbered strips of SAE-1020 steel of uniform size are placed in each still, one in the transfer line, one in the last tube of the outlet furnace and the other in the outlet of the reaction chamber. . . . As soon as a still is shut down, the strips are removed and taken to the laboratory where they are exchanged for new weighed strips which are placed in the still before starting up. At the laboratory the corroded strips are carefully cleaned and weighed; this weight being subtracted from the previous weight.

"The difference in weight divided by the number of hours the still has been on the line is considered the corrosion rate. All of this information together with the average sulphur content of the charging stock, sediment of fuel, pounds of lime per barrel, and various other information are placed on a report which is compared to previous reports before filing. Any change in charging stock sulphur content is usually followed by a change in corrosion rate, which is immediately adjusted by increasing or decreasing the amount of lime as the case may be.

" . . . The plants have given practically no trouble and have done much toward reducing replacement of expensive equipment and give much safer working conditions for employees engaged in process work."

COKE SOFTENING

Although lime was first used in cracking stills for the prevention of corrosion, it was soon found that it was also of great value by reason of its effects upon the character of the coke formed during the distillation. A part of the lime added to high-sulphur charging stock is deposited and carries with it into the coke a considerable quantity of the sulphur from the crude stock. Partial sulphur removal is thus effected, and at the same time the structure of the coke is changed and it is prevented from adhering so tightly to the metal. Such coke, from a run in which lime was used, is much easier to break up and remove from the coke chambers and cleaning out is done much more easily and quickly.

Egloff and Morrell* reporting on this use of lime, said:

"Some of the advantages resulting from the use of lime follow:

1. The heating tubes are more easily cleaned, as the lime apparently yields a protective covering between the steel and coke, preventing its close adherence.
2. The structure of the coke in the reaction chamber is improved so that a smaller amount of fines or breeze is produced in clean-outs and in handling. The coke is more easily broken up in the chamber.
3. The cost of operation will be less than when using caustic soda due to the lower cost of the lime.
4. Corrosion is decreased materially.

"A further and important advantage in the use of lime has been noted in connection with the cracking operation in which the residuum is flashed: The coke formed in the reaction chamber when no lime was used was so dense and hard that it was difficult to remove. By the use of lime as a protecting agent against corrosion, or for the sole purpose of reducing the breaking strength of the coke, this operating difficulty has been overcome.

"The following tabulation shows the analyses of the coke produced by a cracking unit when lime is charged into the system and when it is not charged:

Proximate Analysis	Quantity of lime per bbl. of oil: 0.4 lb.	none
Moisture	2.73%	3.23%
Volatile Matter	11.85	13.28
Fixed Carbon	78.71	81.94
Ash (inclusive of lime)	6.71	1.55
Lime	3.97	...
Sulphur	1.23	0.77
B.t.u.	14,252	15,219

"In the runs in which no lime was used, the removal of the coke from the chamber presented a real problem. The use of lime permitted easy removal of the coke and did not affect its fuel value greatly owing to the increased ash."

B. S. REMOVAL

Just as in the softening of the coke, the lime for this operation is introduced with the charging stock, and so on the flow chart is designated by the same reference letters as for preventing corrosion in still tubes. A part of the lime added to the charging stock is carried over into the settling tank, where it acts both chemically and mechanically to cause a sharper separation and more complete and rapid settling of the bottom sediment. Wastage of oil is minimized and the sediment tends to become more granular—losing considerable of its sticky character and solidifying much more quickly. Handling is made easier and settling time is shortened.

SPECIAL NOTES ON CRACKING

Cracking unit full-scale test runs, observed by the writer, have indicated that four main properties will determine the efficiency of hydrated lime used in cracking units, especially when running high-sulphur crudes. These properties are:

1. *Available Lime Content*—Only available bases will neutralize acidity and prevent corrosion.
2. *Fineness.*—The finer the lime, the better the dispersion will be and the more completely the lime will be utilized. No coarse heavy particles should be present.
3. *Settling Rate.*—A quick-settling lime will tend to deposit too fast in the coke chamber and may cause excessive formation of coke. It may also leave too little lime in suspension for proper settling of B.S. If too slow settling, however, excessive amounts of lime will tend to carry over and may actually retard the rate of settling of the B.S. and cause wastage of oil.
4. *Free Moisture.*—This should be kept at the lowest possible figure, as its presence in hydrated lime seems to cause excessive coke formation. The presence of a small amount of free quicklime in the hydrate will do no harm. (One advantage of using lime in cracking stills is the fact that no water is required as a vehicle.)

If the lime slurry is made from quicklime (as de-

*Before the American Society of Chemical Engineers, St. Louis, December 5-8, 1927.

scribed in Section II), it is important that a dry hydrate be made and that the slurry be passed through a fine mesh screen in order to remove coarse particles as completely as possible.

Table II illustrates the dispersion of lime during the cracking of a high-sulphur crude, requiring heavy lime dosage to prevent corrosion. Samples were taken as indicated and the percentages of calcium oxide shown are the averages of two tests.

TABLE II
Dispersion of Lime in Cracking Unit

Sample No.	SOURCE	Per Cent CaO
2	Limed oil in the still during operation..	0.35
3	Fuel oil going to settling tank.....	1.97
4	Finished fuel oil leaving settling tank..	0.77
5	B. S. drawn from settling tank.....	4.75
1	Coke, after run completed.....	6.45

GROUP III—TREATING

Naphtha Treating

Recent laboratory investigations, small-scale tests and full scale plant runs, looking toward lowering the cost of removing hydrogen sulphide from "sour" naphthas, have served again to emphasize the usefulness of lime as a chemical reagent, and bid fair to result in a considerable saving of production costs. The lime treatment process has passed the experimental stage and is now in regular use by several refineries, each one having developed its own operation controls and details of manipulation.

In general, however, the operation is carried out in a manner practically identical with that previously employed when using caustic as the reacting chemical. Milk-of-lime (made either from quicklime or hydrated lime, as indicated on the flow chart) is substituted for caustic solution, and the circulation or agitation is carried out in standard equipment, with perhaps more attention being given to agitation during the early stages of the absorption. All that is necessary is to provide proper contact between the particles of lime and the hydrogen sulphide, avoiding the presence of too large an excess of lime in the reaction chamber at any one time. If proper concentrations are maintained there should be no emulsion troubles.

The reaction between lime and hydrogen sulphide proceeds in two steps, as indicated by the equations:

1. $Ca(OH)_2 + H_2S = 2H_2O + CaS$
2. $CaS + H_2S = Ca(SH)_2$

Reaction number one produces calcium sulphide which is insoluble in water, but capable of combining with more hydrogen sulphide to form the soluble calcium hydrosulphide, as shown in reaction two. Thus, during the absorption period, there may be present simultaneously calcium hydroxide, which is insoluble; calcium sulphide, also insoluble, and calcium hydrosulphide, which is soluble. The relative proportions of these three compounds present at any given time will depend upon concentrations, temperature, amount of agitation, rate of throughput, etc., and these factors must be worked out to suit local conditions, if the greatest efficiency is to be secured. (By proper contacting and agitation it has been found possible to completely exhaust the lime and secure an entirely water-soluble reaction product.)

POSSIBLE ALTERNATE METHOD

It has been found that hydrated lime may be used in the dry form for neutralizing hydrogen sulphide in naphtha, thus offering the possibility of avoiding the handling of large volumes of water, and eliminating any danger of emulsions. The absorption of H_2S may be accomplished by injecting a lime-naphtha slurry into the main stream of sour naphtha as it enters a suitably arranged system of mixing, agitating, reaction and settling chambers. Perhaps a counter-flow system could be used, whereby the partially spent lime could be completely utilized by in-coming fresh stock and fresh lime used to complete the removal of H_2S from the out-going naphtha. Complete data as to rate of absorption, agitation required, etc., are not yet available, but it is believed that this proposed method of H_2S removal offers interesting possibilities that may more than repay the cost of detailed investigations.

GASOLINE SWEETENING

Gasoline sweetening is another recently developed use for lime, offering a saving over the costs of other processes. The process involves the use of calcium plumbite instead of sodium plumbite, the active calcium compound being continuously regenerated and the use of water being restricted to a very small required minimum. For a detailed summary of this process see page 168 of the Process Number of The Refiner and Natural Gasoline Manufacturer issue of February, 1932, Vol. 11, No. 2.

The hydrated lime for this operation should be as high in Available CaO as possible and of extreme fineness, so as to secure complete dispersion throughout the mass of the porous mineral used as a carrier.

NEUTRALIZING EXCESS ACIDS

A very obvious use for lime which requires little space here is neutralizing excess acids. The choice between milk-of-lime and lime slurry (from either quicklime or hydrated lime) will depend primarily upon their relative costs, though in some cases it

may be undesirable to introduce water into the system, in which case only the slurry would be used.

GAS SCRUBBING

Test runs made in a full-sized plant installation by M. E. Schulz, chief engineer of the Gulf Refining Company, (Paragon) Toledo, Ohio, have definitely established the superiority of lime as an effective reagent for the removal of hydrogen sulphide from gases collected from various storage, distillation and cracking operations, and have proven its economy from an investment standpoint.

These tests developed the following information:

1. The cost of the lime required to remove a given amount of hydrogen sulphide was less than one-fifth of the cost required for caustic soda to remove the same quantity of this corrosive gas.

2. Whereas a solution of caustic soda gradually loses its efficiency from the beginning of the absorption until the point of saturation is reached, a milk of lime suspension retains its full efficiency and absorbs hydrogen sulphide at a constant rate up to its saturation point.

3. The absorption was more complete with lime —1.03 pounds of lime removing as much sulphur as 1.14 pounds of caustic soda, and the scrubbed gas carrying less sulphur than when soda was used.

4. When using caustic, it is necessary to have quite extensive installations of counter-flow apparatus, together with circulating pumps which must be maintained and operated continuously. With lime it is only necessary to provide a mixing tank for fresh batches of lime, and to lead the raw gas into the bottom of the absorption chamber and let it bubble up through the milk of lime suspension. Exhaustion of the lime is readily indicated by a lead acetate test of the scrubbed gas, and a fresh batch of milk-of-lime can be introduced in a few minutes. Aside from that required for making up and transferring fresh batches of lime, no power-consuming equipment is needed.

Mr. Schulz also notes that, while the agitation effected by the in-coming gas is required to keep the lime in suspension while the absorption is proceeding, the final reaction product is a practically clear solution that can be easily drawn off for disposal.

While not mentioned in the report of Mr. Schulz, it is worth noting that a very simple apparatus could be constructed for this gas scrubbing operation. This would consist of two absorption chambers in series, each one being provided with a water inlet and an opening for charging of fresh batches of lime, and being fitted with a drain cock and a small agitator driven by an independent clutch from a centrally located motor. The first chamber would remove 90 to 95 per cent of the hydrogen sulphide and the second one would probably remove a majority of the remainder. When the lime in the first scrubber became saturated, it would be taken off the line, the spent lime solution drawn off through the drain cock and a fresh batch of milk-of-lime made up by means of the agitator. During this time the gas would be passed through the other absorber and when the fresh unit was cut in the flow of gas would be reversed from its former direction so as to exhaust the oldest lime first. Such an arrangement as this would provide the most efficient H_2S removal with a small investment for equipment and at the lowest cost for chemicals, labor and maintenance.

GREASE MANUFACTURE

The manufacture of greases, in common with many other emulsification processes, is continually being developed from an art into a science. New types of greases are constantly being demanded by other industries and new compounds or mixtures are being produced to meet these new requirements. Programs of research and experimentation are adding to the available knowledge of the properties and functions of the separate ingredients entering into the manufacture of emulsions in general, and are increasing the usefulness and improving the quality of petroleum greases. Various oils and fatty acids are used to combine with a number of metallic bases to form a great variety of soaps—these soaps, used singly or in different combinations, accomplishing the emulsification and also conferring diverse qualities and properties upon the finished products.

Open kettles and pressure cookers are employed and a great variety of soaps is now made for special purposes, but lime soaps have always been, and will probably continue to be, the ones most generally used, both on account of low cost and desirable chemical and physical properties. These lime soaps, like all other ingredients used, have received a great deal of attention from grease-plant operators and chemists, and the proper grades of lime to be used, as well as their correct utilization, are now much better understood than they were when all greases were made by rule-of-thumb methods only.

The use of a special hydrate for grease making is indicated on the flow chart because requirements are more exacting than for other process operations, and because it is essential that the lime specification be rigidly adhered to if the quality of the product is to be maintained. Fundamental specification requirements for grease-making lime are:

1. Purity. In addition to a high percentage of available CaO, the lime should contain a minimum of total impurities, and particular attention should be given to the possible harmful effects of any one, or more, of such impurities as are present.

2. Degree of Hydration. The lime should be completely hydrated, with only small allowances for free moisture.

3. Fineness. The finer the better, since the time

required for saponification will depend upon the rate of reaction, which is in turn governed by the surface area of the lime.

4. Uniformity of Composition. Percentages of individual impurities, as well as of CaO, should be as uniform as possible from one cargo to the next. This will insure uniformity of both yield and quality of grease from one batch to the next.

5. Freedom from Grit. This requirement is perhaps the most important of all, since a mere trace of hard, gritty material may ruin an otherwise perfect batch of grease. The lime should be entirely free from all grit.

GROUP IV—POWER, MECHANICAL, ETC.

Water Softening

So much was said on the subject of water softening in Parts I and II of the series that we only need mention here the factors that determine the quality of lime for this use. Either quicklime or chemical hydrate may be used, as indicated on the flow chart, and the lime should be valued according to available CaO or $Ca(OH)_2$; kind and amount of impurities; rate of reaction; fineness, and settling rate.

CONSTRUCTION

The application of lime to miscellaneous construction work, involving the use of mortar, plaster, stucco and concrete, are well known to most refinery engineers. It is, however, worth noting that in many types of construction work numerous economies can often be effected by a more generous use of lime than has sometimes been practiced.

Advantage may be taken of the fact that masonry work laid up in mortar based on certain lime-cement mixtures is stronger than if a straight cement mortar were used, as well as being considerably cheaper. Or it may be of benefit to know that hydrated lime is one of the best integral water-proofings for concrete. These and many other important construction facts will gladly be explained in detail by the National Lime Association, Washington, D. C., or by individual lime manufacturers and engineers.

Bulk quicklime and masons hydrated lime, conforming to current specifications of the American Society for Testing Materials, are available everywhere, and should be handled and used in accordance with instructions from their manufacturers. Chemical hydrates and special hydrates (such as finishing limes, etc.) may be advantageously used in many construction jobs and, wherever applicable, are almost certain to be economical and decidedly worthwhile.

SANITATION

Whitewash may be used to good advantage in many ways, such as for protecting wooden structures from decay; promoting safety of workmen by increasing the visibility of obstructions; brightening up the interior of buildings, and in numerous other ways. Formulas are available covering its preparation from either quicklime or hydrated lime; for interior or exterior use; plain or washable; harmless or poisoned; glossy, dull or tinted, and it constitutes the cheapest form of paint for the uses for which it is recommended.

Nor should the sanitary value of lime be overlooked, whether it be used in the form of whitewash to promote general cleanliness or as a spray or dust (alone or in combination with other materials) to control mosquitoes, flies, bugs and vermin, or to kill bacteria and prevent the growth of molds, algae, etc.

In connection with first-aid work, a special memorandum should be made that plain lime-water is an excellent remedy for burns. Applied promptly and generously, it has been known to completely counteract the effect of a direct flame on the skin—taking out all soreness and preventing any blistering.

Any ordinarily good lime will be satisfactory for some of the sanitary uses indicated above, but the better grades of hydrate may be required in the preparation of certain special sprays, dusting powders and medicinal preparations.

NEUTRALIZING ACID SLUDGES

Most refinery wastes are acid to a greater or less degree and carry in solution or suspension a variety of materials which, in some cases, may cause serious stream pollution or other nuisance if allowed to leave the refinery as they are. As with many other industrial wastes, the oil refinery effluent may often be rendered entirely harmless by suitable chemical and mechanical treatment, since after all it is only a highly polluted water—perhaps a little worse than that used as a municipal supply by some large city purification plant. Lime is the cheapest alkali available for neutralizing acids, in addition to which it may frequently be used to precipitate soluble compounds and flocculate colloidal substances held in suspension. Such precipitated or flocculated material may then be removed by mechanical sludge removers, filters, or by sedimentation, leaving a clear effluent that is neutral or slightly alkaline and may be discharged with perfect safety to any watershed or drainage system.

Special problems will arise at different refineries, and special treatments will have to be developed to solve them, but it is well to give careful consideration to the service that may be rendered along this line by lime.

Role of Oxygen... *in the* CONVERSION OF Hydrocarbons

I. N. BEALL
Chemical Engineer

THE fact that oxygen in either the free or combined form has a marked effect upon petroleum products has been known for a great many years. As early as 1865 Gesner[1] noted and reported the action of air on organic substances and hydrocarbon oils at high temperatures. In 1868 Bolley[2] noted the absorption of oxygen by paraffin wax at 300°F. W. P. Jenney[3] in 1876 obtained a patent for treating acid sludge at 48°F. with a current of air.

Patents for the oxidation of coal tars and petroleum residues by the use of oxidizing agents such as potassium permanganate and permanganic acid in admixture at 300°F. were issued to De Smedt[4] in 1881. Schall[5] discovered that a well divided stream of oxygen blown into paraffins, vaseline and heavy mineral oils—admixed with manganese compounds, heated to 285°F. to 302°F. resulted in their practically complete oxidation.

Salathe[6] proposed a process for blowing heated air through asphalt either with or without admixture with manganese dioxide and/or litharge. Zaloziecki[7], Engler and Bock[8] and others detected and reported that when air was passed through hot mineral oils small amounts of simple fatty acids such as for example, acetic acid resulted. Holde[9] noticed that when thin layers of mineral lubricating oils on metal surfaces were heated at 212°F. in the presence of atmospheric air for 10 hours that oxidation caused their thickening and an increase of viscosity.

Perhaps the best known process is that of F. X. Byerly[10] for the production of "byerlite," an artificial asphalt of considerable commercial importance. By this process air is drawn through petroleum residues at 400°F. to 600°F. over a period depending upon the physical properties desired in the finished product. As this reaction was strongly exothermic, the temperature would raise during the blowing period from 400°F. at the beginning to as high as 750°F. without the aid of external heat. The oxygen content of those "byerlites" was low (1.90 to 2.20 per cent) by reason of the fact that the oxygen combined with the hydrogen of the hydrocarbons substances and was removed as water in the form of steam. It is logical to assume that the increase in "unsaturation" was a contributing factor in the resultant condensation and polymerization to tarry and asphaltic materials.

At lower temperatures than those used by Byerly and Maberry the formation of intermediate products such as alcohols, aldehydes, ketones are considered to occur, which on further oxidation result in fatty, napthenic and other organic acids. Brooks[11] states, "such intermediate products are undoubtedly formed, which may condense with the formation of water which is always observed."

It would seem reasonable to assume from the foregoing that, in so far as heavy oils, waxes, residuum, etc. are concerned, the effect of oxygen is to produce partial oxidation products at low temperatures (300° F.) and substantially atmospheric pressure, whereas at higher temperatures (400°F.—750°F.) the effect is to produce resinification and asphaltization by the splitting off of hydrogen.

OXIDATION OF THE HIGHER PARAFFINS

Apparently most of the work done on the oxidation of the higher paraffins was done in Germany previous to and during the late war. Bolly and Tuckschmidt[12] in 1868 state that paraffin wax is oxidized by air at 250°F. to 300°F. Many conflicting claims are made as to the use of various metallic catalysts but the indications are that the product from a previous oxidation was the most effective factor for the initiation and promotion of such reactions. Löffl[13] noted that air under pressure favorably influenced the reaction and Schneider[14] made use of pressures up to 350 pounds per square inch. Grun[15] isolated from such partially oxidized products, esters of the fatty acids and higher alcohols. Yields, as high as 86 per cent of theory of the fatty acids, have been reported at 250°F. and 275 pounds per square inch pressure. The use of elevated pressure obviously accelerated the reaction and permitted the use of a temperature 50°F. lower than that used at atmospheric pressure.

Engler and Weissberg[16] call attention to the fact

THIS is the second of a series of articles dealing with oil-gas conversion, decomposition, oxidation, synthesis and conversion as applies to the processing of natural gas and oil. The ground work or introduction for this series was presented by the author in two articles last year, appearing as "Molecular Arrangement and Rearrangement of the Natural Gas Hydrocarbons," issue of November, 1931, page 95, and "Oxidation of Natural Gas Hydrocarbons" appearing in the issue of December, 1931, page 94.

The first of the series applying specifically to such synthetic processes appeared last month in this column, page 390. "Notes on Oil-Gas Conversion." In this present work Mr. Beall carries the study much further than the broad general concept and in addition to citing numerous references and results of previous investigations outlines certain possibilities of application of later knowledge. Additional information pertaining to the oxidation of gaseous hydrocarbons and the interaction of oxidized hydrocarbon material with unoxidized hydrocarbon material will be presented in later articles.

that organic substances which are ordinarily resistant to oxidation, may be rather readily ovidized in the presence of a substance of itself capable of direct oxidation. Such intermediate oxidation agents are thought to pass through the organic peroxide stage; these peroxides, then by their reactive nature, effecting the hydrocarbons which are relatively inert, causing them to become oxidized.

Recent investigations seem to bear out Engler's contention as to the formation of organic peroxides as one of the initial stages in the oxidation of hydrocarbons. In this way the organic peroxides are able to bring about the oxidation of the saturated hydrocarbons. Engler and Weissberg state, "oxygen combines as molecular oxygen" and "a peroxide is formed which may then re-arrange to ordinary oxides or may react upon other unoxidized substances." These investigators isolated a number of these organic peroxides in a fair state of purity.

CRACKING IN THE PRESENCE OF OXYGEN

Most of the earlier methods proposed for the use of atmospheric oxygen in oil cracking systems are the result of attempts to supply heat by means of restricted internal combustion of portions of the hydrocarbon material undergoing treatment. Aside from this, certain benefits result in the way of prevention of carbon deposition on the metal surfaces. Also there are the chemical effects of restricted oxidation. The metallic oxides have been largely used as "transfer" agents for oil oxidation and cracking. Hirschberg[17] reported passing 100 kilograms of kerosene of a specific gravity of 0.825 over chromium oxide heated to dull redness at a pressure of approximately 15 pounds per square inch and thus obtaining 81 per cent by weight of liquid boiling below 338°F. The specific gravity of the recovered liquid was about 0.720. On this basis, the volumetric yield would be about 92.8 per cent which is considerably better than that obtained from present industrial cracking processes. It would seem as though such yields would be worthy of further investigation.

According to A. S. Ramage[18] hydrocarbon vapors, when passed over reducible metallic oxides, are converted into olefins, terpenes, napthenes and aromatics of low boiling range. Ramage considered that the conversion of paraffin into olefin, of olefin into terpene, and of terpene into aromatic, was the result of restricted oxidation, hydrogen splitting off to form water. Iron oxide (Fe_2O_3) is mentioned as a suitable catalyst or oxidizing agent when used at temperatures of 1076°F. to 1382°F. and atmospheric pressure. The iron oxide is stated to be reduced to the lower oxides, Fe_3O_4, and FeO, and Fe by the hydrocarbon vapors. Yields of 90 per cent condensate yielding 77 per cent boiling below 356°F. are reported.

Another interesting vapor phase method is that proposed by Mann and Chappell[19] for the dehydrogenation of petroleum distillates. This process operates at sub-atmospheric pressure and is stated to give high yields of the aromatic hydrocarbons. About 15 gallons of cracking stock to 500 cubic feet of air is passed over porous material impregnated with the oxides of metals such as nickel and copper on broken firebrick at temperatures from 1112°F. to 1382°F. It is claimed that 40 to 75 per cent of liquid aromatic hydrocarbon is produced by this treatment together with 20 to 45 per cent of fixed gases. In addition to the processes mentioned here, many other methods have been proposed for the cracking of oils at atmospheric, sub-atmospheric and slightly elevated pressures and at high temperatures in the presence of oxidizing agents. The majority of the proposed processes operate in the vapor phase.

DECOMPOSITION OF OXYGEN CONTAINING COMPOUNDS AT HIGH TEMPERATURES AND PRESSURES

The literature contains but little information on the decomposition of hydrocarbons in the presence of oxygen at high temperatures and pressures. Herndon and Reid[20], however, conducted a series of experiments with bombs using a procedure somewhat similar to that used by Cross in making equilibrium cracking tests on oils. In these tests, various pure

organic compounds were used such as the alcohols, aldehydes, ketones, organic acids and other oxygen containing compounds. Both the gaseous and the liquid products of these equilibrium tests were examined and analyzed. Methyl alcohol, when heated to temperatures of 752°F. to 887°F. in a bomb for two hours, decomposed into gases having the following composition:

CO_2	8.1 per cent
CH_4	41.8 per cent
C_2H_4	0.8 per cent
CO	3.1 per cent
H_2	39.4 per cent

At 752°F. a charge of 60 grms. yielded 39 grms. of liquid boiling range 147°F. to 212°F. and 10 liters of gas. At 842°F. for two hours 60 grams yielded 20 grams of liquid and 15 liters of gas. The liquid was mostly water. At 887°F. and two hours heating there was 48 grams of liquid, boiling range 147°F. to 210°F. Fifty-nine grams of ethyl alcohol (C_2H_5—OH) on heating for two hours at 797°F. in a manner similar to that used for methyl alcohol yielded a liquid that separated into an upper layer of 17 grams and a lower layer of 15 grams and 14.5 liters of gas. Under the same conditions as above, but at 860°F. the upper layer amounted to nine grams, the lower 15 grams and there was 19 liters of gas. The boiling range of the upper or oil-soluble layer is stated to be 64°F. to 518°F. and that of the lower 86°F. to 216°F. An analysis of the gases is given as follows:

Carbon Dioxide CO_2	10.2 per cent
Methane CH_4	31.8 per cent
Ethylene C_2H_4	8.0 per cent
Carbon Monoxide CO	7.6 per cent
Ethane	36.6 per cent

The authors consider that the general reactions for the decomposition of alcohols are those of dehydrogenation, dehydration and polymerization of the hydrocarbon residues. The higher alcohols also yielded two layers of liquid product when heated in the bomb in a similar manner to that used for methyl and ethyl alcohols. Secondary butyl was found exceptional in that no gaseous product was obtained. Tertiary butyl alcohol was almost completely decomposed when heated at 752°F. for two hours, yielding nearly the theoretical quantity of water. The end point for the distillation of the upper or water-insoluble layer is higher for the ethyl alcohol decomposition product than that of the higher alcohols. This may be of significance in that it shows that the ethylene produced by the primary dehydration ($C_2H_4OH \rightarrow C_2H_4 + HOH$) has a greater tendency towards polymerization than do the higher unsaturated hydrocarbons produced from the dehydration of the higher alcohols.

"In these tests benzene was found to be relatively stable even when heated to 932°F. for two hours. Heptane underwent slight decomposition at 752°F. for two hours yielding some gases and heavier liquids resembling lubricating oil. The organic acids also break down when heated under equilibrium pressure and with the exception of acetic gave the water-insoluble layer and the water-soluble layer. Acetaldehyde (CH_3CHO) at 635°F. for two hours gave 33 1/3 per cent upper layer and about 29 per cent lower layer and two liters of gas from 60 grams. The upper layer of the liquid product had a boiling range from 131°F. to 680°F. and the lower liquid layer from 174°F. to 212°F. "Benzaldehyde" at 400°C. for two hours gives benzene as the principle product as well as other higher boiling products."

Various other organic compounds, among which were the alcohols, aldehydes, ethers, glycols, aromatic and aliphatic hydrocarbons, etc., were heated at constant volume at temperatures from 482°F. to 977°F. The reader is referred to the original article for further details as to the methods used and the results obtained. The results obtained with the organic compounds containing oxygen are of particular interest to this discussion in that they show the relative ease with which such compounds decompose when heated at constant volume yielding complex mixtures over a wide boiling range. While the reactions are primarily those of dehydrogenation, dehydration and synthesis using as a raw material pure organic compounds, the resulting products appear to be somewhat similar to those obtained by the hydrogenation of carbon monoxide by the "Synthol" process. In both cases, complex mixtures of wide boiling range are obtained which are partly water-insoluble.

A general reaction for the Synthol Process is given as

$$nCO + 3nH_2 \rightarrow CnH_{2n+2} + nH_2O$$

By the Patart Process,[21] carbon monoxide and hydrogen are made to combine under pressure and in the presence of a catalyst to form methanol

$$CO + 2H_2 \rightarrow CH_3OH$$

Peytral[22] and Ipatiev[23] consider that the decomposition of methanol takes place as follows:

$$CH_3OH \rightarrow H_2 + H.CHO$$
$$H.CHO \rightarrow CO + H_2$$

Herndon and Reid seem to check with the above in that they state that methyl alcohol gave exceptional results in that no liquid hydrocarbon or insoluble portion was obtained, the products of decomposition being gaseous with the exception of water. In other words we are here dealing with a reversible reaction and conditions of shifting equilibrium where carbon, hydrogen and oxygen may be made to assume various molecular forms depending upon the time, temperature, pressure and catalysts.

The reactions between air (oxygen) and saturated hydrocarbons offer a means for introducing a series

of reactions somewhat resembling those obtained by the decomposition of organic oxides and syntheses involving the use of carbon monoxide and hydrogen. Various investigators have noted the formation of formaldehyde and unsaturated hydrocarbons on the incomplete combustion of the saturated hydrocarbons. Stepski[24], subjected hexane and isopentane fractions to incomplete combustion and obtained water, carbon dioxide, carbon monoxide, ethylene, propylene, butylene and amylenes in small quantities. Chemical oxidizing agents have been shown also to react with the saturated hydrocarbons. Zelinsky and Zelikow[25] found that a one per cent solution of potassium permanganate oxidized $(C_2H_5)_2CH.CH_3$ and that the reaction was more or less general for the type R_2CHR of hydrocarbons. Meyer and Saam[26] found that methane and ethane are very slowly oxidized by five potassium permanganate solutions. The presence of the unsaturated hydrocarbons has been noted to influence the oxidation of the saturated hydrocarbons.

It is probable that the oxidation of the unsaturated hydrocarbons takes place first and then a secondary reaction takes place between the oxidized unsaturate and the saturate. However, as has been previously discussed, the introduction of a previously oxidized hydrocarbon product seems to promote the reaction between oxygen and the paraffins. Kishner[27] found that while 2.6-dimethyl octane was fairly stable to permanganate at 212°F. in the presence of menthene (unsaturated) the reaction was rapid at 122°F. Various other oxidizing agents, such as nitric acid, nitrogen peroxide, alkaline permanganates, chromyl chloride, lower oxides of nitrogen, etc. have been used to advantage. Granacher states that paraffin wax is slowly oxidized by nitrogen peroxide between 230°F. and 302°F. producing a series of fatty acids beginning with acetic. The reaction between paraffin wax and strong nitric acid is violent at 212°F. Apparently the generic term paraffin is without significance in the examples cited as the oxidation reactions seem to be more or less general for the type. The product of oxidation is not necessarily an organic compound containing oxygen, but may be an unsaturate or a polymer of the unsaturate.

The water-insoluble, oil-soluble layer resulting from the decomposition of various oxygen containing organic compounds on pyrolysis at constant volume substantiate this view point. The present industrial processes for the production of ethylene by the pyrolysis of ethyl alcohol over catalysts at atmospheric pressure are typical for the alcohol series.

ACTION OF WATER ON HYDROCARBONS AT ELEVATED TEMPERATURES AND PRESSURES

A number of processes have been patented covering the interaction between steam and petroleum products at elevated temperatures and pressures. The Greenstreet[28] Process at one time attracted considerable attention. One method of procedure mentioned was to atomize a heavy oil with steam at 100 pounds pressure and pass the resultant mixture through a coil of pipe heated to a cherry red heat. The gasoline product was said to contain about 40 per cent of the olefins and to be uniform in quality. It is claimed that there is practically no formation of fixed gases and carbon when this process is properly operated and that the inner surface of the heating coils soon become covered with an enamel or smooth coating of magnetic oxide of iron. At the temperatures used it is likely that the steam would react with carbon, hydrocarbon or iron to form oxides and that hydrogen would be liberated.

$$C + H_2O \rightarrow CO + H_2$$
$$3\,Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
$$CxHy + nH_2O \rightarrow C_xH_yO_n + nH_2$$

It is claimed that alcohols also may be produced by a somewhat similar treatment of crude oil fractions with steam. By cracking a hydrocarbon oil of 32° — 50° Be. at 800°F. to 1500°F. and 80 — 125 pounds per square inch, a colorless gasoline substitute of 50 — 52° Be. is said to be produced by distillation having an end point not higher than 410°F. The synthetic crude before fractionation had a sweet odor and a redish color. The distillation residue was used for recycling to produce a further yield of light product.

The Greenstreet Process is only one of a large number of processes proposed for cracking oil in the presence of steam. Zerning[29] sprayed oil and water into tubes heated to 572°F. The mixture from the first tube section was then passed into the second tube section heated to 932°F. and from thence to a final tube section heated to 1292°F. A pressure slightly above atmospheric is stated to yield the best results. Products of high chemical activity are said to be produced. Light hydrocarbon gases are also produced by a modified procedure in which the tubes are coated with fire-clay, the temperature in first section being kept between 572° — 752°F. and the second and final section at a dark red heat.

A rather interesting process consists in preparing an emulsion of crude oil or a fraction thereof with water using an emulsifying agent and then forcing the emulsion at three to six atmospheres through a retort packed with iron, steel or nickel shavings and heated to 500 to 900°F. Nascent hydrogen is said to be produced by this treatment and a considerable conversion into light oils suitable as motor fuel.

Another interesting procedure has been described by E. L. Davies[30] for the preparation of light hydrocarbons from heavy oil by passing the vapors admixed with steam through tubes packed with iron or steel shavings. Benefit by the way of increased yields resulted from increasing the pressure. Pressures as high as 100 pounds were used with temper-

atures between 1202°F. to 1247°F. A gasoline of 72° Be. was produced.

In all the methods proposed for processing oil with steam for the recovery of light hydrocarbons, the reducing properties of steam on carbon and hydrocarbon material has apparently been overlooked. It is probable that a considerable proportion of the effect attributed to the reduction of water by metals to form the corresponding metallic oxides was due to reduction by carbon and hydrocarbon.

In the process discussed by the writer for the conversion of oils the easily reducible organic oxides are used. (Refiner & Natural Gas Manufacturer, June, 1932, page 390). Water is a very thermo-stable compound as compared to the organic compounds containing oxygen and because of this fact very extreme temperatures must be used to effect its decomposition and cause its reaction with a petroleum oil. The lower temperatures made possible by the use of hydrocarbon oxides instead of steam permit the use of higher pressures and its beneficial effects. The use of an inert gas such as nitrogen establishes the vapor phase under pressure thus giving a uniformity of reaction not possible in the liquid phase. When nitrogen is used it also apparently becomes "activated" and exerts a beneficial effect upon the conversion products. Additional information pertaining to the oxidation of gaseous hydrocarbons and the interaction of oxidized hydrocarbon material with unoxidized hydrocarbon material will be given in a subsequent article.

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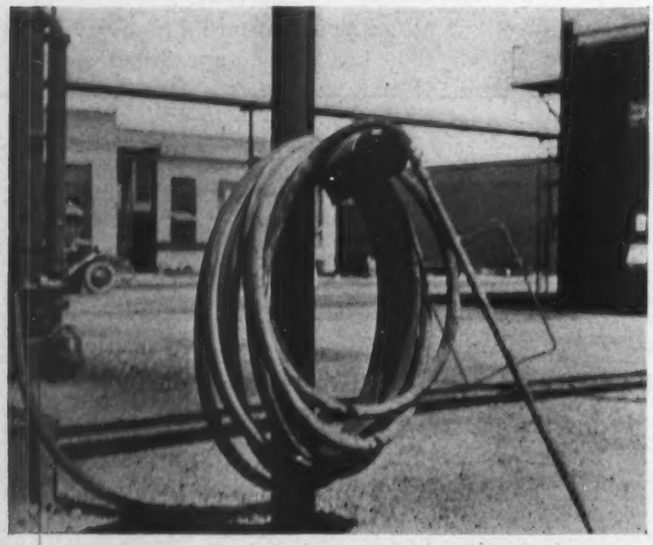
Cleaning Tubes in Heat Exchangers

CLEANING tubes in condensers and heat exchangers is an agyravating process to the majority of plant operators. After the heads have been removed, the tubes are usually cleaned before any other part of the apparatus is placed in condition for reassembling. Steam or hot water is used in most plants to flush out the tubes, and without some kind of handling device, the nozzle gets uncomfortably hot to the hands even if thick gloves are worn. sometimes even gloves are a nuisance, soaked with hot water, the rate of heat transfer from the nozzle to the skin is painfully noticeable. Burlap bags are sometimes resorted to in overcoming the heat, but with this extra bundle around the nozzle, the efficiency of the operator is impaired.



Pipe Handles welded on to facilitate steaming and cleaning tubes with hot water when reconditioning tube and shell exchangers and condensers in the plant of the White Star Refining Company at Trenton, Michigan.

To provide for efficient work carried out with speed and dispatch, and at the same time taking into consideration the welfare of the employees, White Star Refining Company at its plant near Trenton, Michigan, has made several nozzles from ordinary pipe. Near the hose connection to which the nozzle is attached a pair of bails or hand holds are welded wide enough and from material of sufficient strength that the operator may use both hands in running the nozzle through the tubes when cleaning out. The chance for burned hands is eliminated when the operator can operate the cleanout tool with both hands, and the knowledge of safety which he has enables him to speed up the work of cleaning.

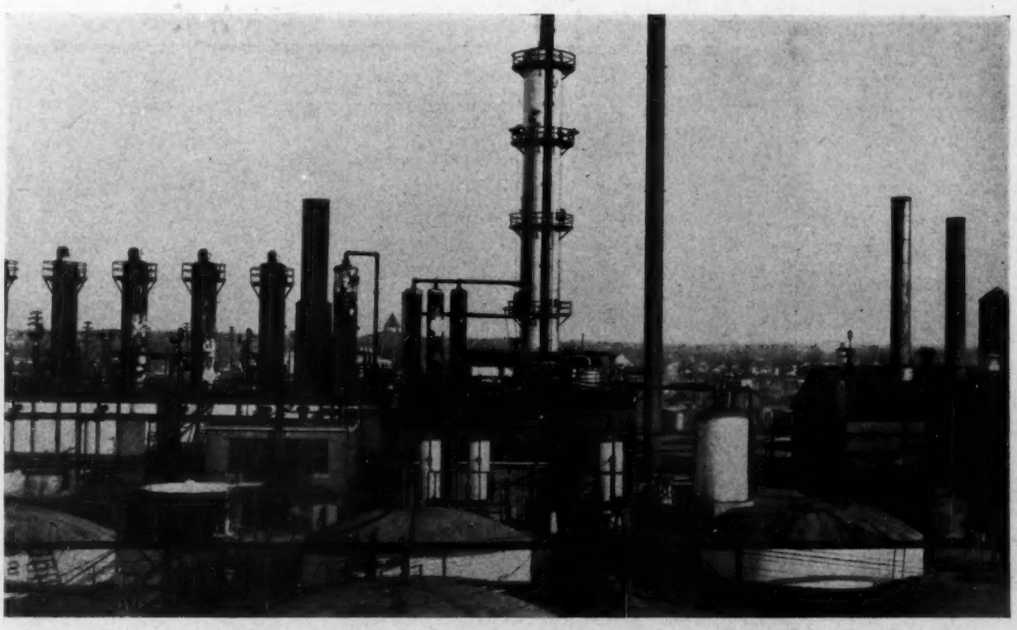
Modern Equipment *Increases* Plant Efficiency

PROOF that tube still skimming with bubble tower fractionation is superior to the older methods of either batch or continuous shell still refining has been shown on the balance sheets of many refineries through the continuous uninterrupted service that this type of equipment has given them. Sloppy cuts have been eliminated to a marked degree, and if the columns are placed in the proper equilibrium, overlapping of fractions is scarcely noticeable.

Installing a 6000-barrel unit of this type, designed by Winkler-Koch Engineering Company, in 1929, Producers & Refiners Corporation in West Tulsa has operated it over two years without difficulty in making sharp cuts of the various products desired. Once on stream and the unit in balance, it requires practically no supervision.

The stock charged to this unit is Mid-Continent crude with an average gravity of 39.5° A.P.I., which is picked up from storage by a Worthington two-inch centrifugal pump running at 3600 revolutions per minute. The pump is designed to deliver 175 gallons per minute against a total discharge head of 500 feet. Driven by an Allis-Chalmers 440-volt, 50-horsepower, alternating current motor running at 3600 revolutions per minute, it will deliver under these conditions a crude feed of 250 barrels per hour through the tube still.

Following the flow, the crude after it leaves this pump is carried through a four-inch line leading to a pair of Braun vapor-to-crude heat exchangers placed on a steel platform just above the upper rim of the conventional condenser box. The rate of flow is governed by a Brown automatic flow controller placed in this line which permits only a predetermined quantity of crude to be charged to the unit. After the crude passes through the tubes of these exchangers, where it is heated to 180° F., it is led through an insulated six-inch line to the dehydrator or water settler. An old Dubbs 10 x 15 reaction chamber was utilized for this part of the equipment, being set on concrete piers outside the control room. Entering through the upper head, the oil is carried through an extension of the six-inch line to the bottom of the drum, then by flowing upward to the outlet, also placed in the upper head, it drops out the free water before passing through the



View of the 6,000-barrel skimming unit in the plant of the Producers & Refiners Corporation, West Tulsa, Oklahoma.

other sections of the unit. Water that has been separated from the charge is removed from the bottom head through a Fisher float controlled valve. The dehydrated oil after it leaves the upper connection is carried through an insulated six-inch line to the main heat exchanger bank. Five of these Braun units are placed so that the flow is in series, the fresh charge flowing through the tubes while the hot residuum from the fuel oil stripper column passes through the shells. Counter-current flow is maintained, and as the oil leaves the last exchanger it is at a temperature of 330° F.

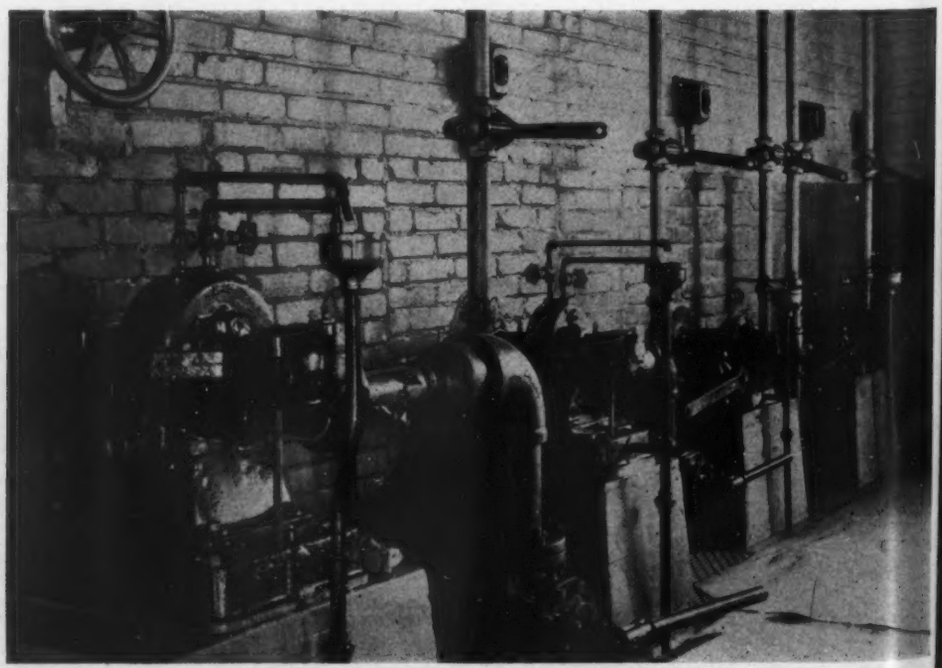
Directly from these exchangers, the crude is carried through an insulated line placed underground leading directly to the tube still. It enters the lower section of the vertical bank, flowing upward through 20 sections, then led outward and up to the twenty-first section. The twentieth and twenty-first section are separated a sufficient distance that four sections of superheated steam tubes could be set in. Leaving the twenty-sixth section, the oil is led to the roof bank, where it is heated to 600° F. Carried through the transfer line, the oil is flashed directly into the main fractionating tower at a point approximately 30 feet from the concrete base.

Entering this tower, which is eight feet in diameter by 96 feet in height, carrying 30 plates, the oil is distributed on the first bubble or stripping tray. Steam is conducted through an eight-inch header to the four sections, where it is superheated in the tube still. Carrying an average temperature, a part of this steam is introduced in the transfer line just before it is connected to the column and enters the column at the same time as the crude is flashed. Practically all the desirable constituents of the fresh charge are separated from it in this operation.

Residuum flows through a six-inch line into the fuel oil stripper tower placed beside the main column and resting on a concrete slab level with the surface of the plant yard. A portion of the superheated steam is injected into the mass of oil near the base of the tower, driving from it those fractions which may have been carried on with the flow of oil. Seven stripping trays are placed in this tower, over which the residuum is forced to travel before entering the base of the column. The stripped crude is now termed "Dubbs charging stock," and has a temperature of 500° F. as it enters the residuum pumps. These are Worthington 10 x 6 x 10 duplex steam pumps, equipped for hot oil service. A Brown automatic controller regulates the speed of the pumps to conform to the amount of residuum handled by them, and the level in the stripper column remains the same regardless of the amount of charging stock fed to the unit.

As these pumps remove the hot oil from the column, it is transferred directly through the Braun exchangers, where the temperature is reduced to 235° F. Leaving them, it is led to the proper storage, from which it is picked up by the charging pumps at the Dubbs cracking units as it is needed. The vapors arising from the fuel oil stripper are conducted back to the main fractionating tower through a six-inch line to be refractionated for the lighter constituents carried back. The fuel oil removed from the side stripper averages 25.5° A.P.I. gravity, and represents approximately 47.5 per cent of the crude charge passed through the unit.

The vapors removed from the crude as it is flashed into the main column all travel upward through the tower where, in passing through the first five fractionating trays, the distillate is condensed and removed as a side stream. Refluxing at this point is by hand control. A six-inch and 1½-inch by-pass was installed so that a part of the distillate could be drained back to the bubble caps as needed. The six inch control is



Charging and Reflux Pumps

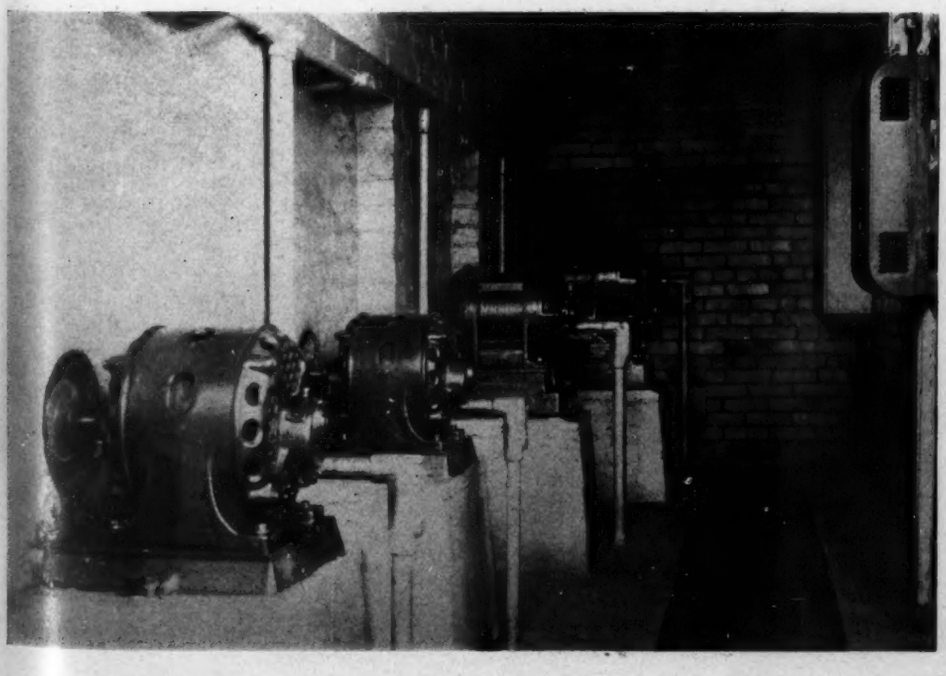
opened to a rough adjustment, while the finer adjustment is made through manipulation of the 1½-inch by-pass line. Rods hanging downward from these gates, which have geared wheels, enable the operator to make the adjustments from the ground.

The side cut of distillate is conducted through a three-inch line to the side stripper placed on a steel platform level with the vapor-to-crude exchangers and near them. This column has seven stripping trays over which the distillate flows to the base to be agitated by more superheated steam. Those fractions driven from the base upward are conducted back to the main column through a four-inch line for further fractionation. The finished distillate flows from the side stripper through submerged cooling coils and thence to the proper storage. Approximately three per cent of the original charge is removed to form this product.

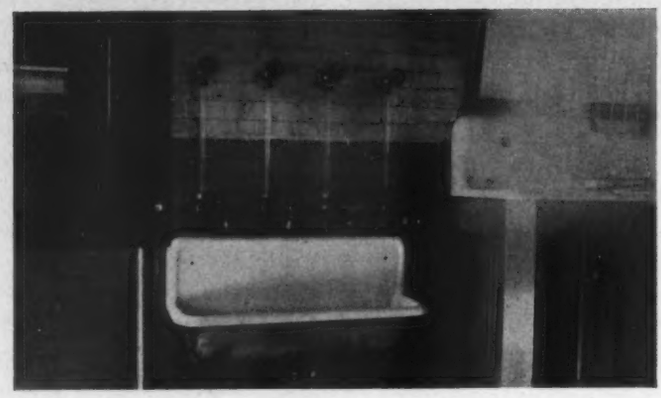
That part of the vapor content of the crude which is not removed as distillate passes upward through an additional nine bubble trays to a point where the kerosene fraction is removed. A temperature of 465° F. is maintained at this point to control the quality of the product. The cut is taken from the side of the tower through a three-inch line and is led to another side stripper, identical in construction with the distillate tower. Falling to the base, it is agitated with superheated steam, as in the distillate column, but is removed through condenser coils to a reflux drum where a portion of it is picked up by a two-inch Westco turbine pump driven by a two-horsepower Century 440-volt motor. Led through a 1½-inch line the reflux is discharged into the tower to maintain close fractionation of the kerosene side cut. Vapors from the side stripper flow back to the main column through a four-inch line. The finished kerosene flows from the reflux drum under process pressure to the proper rundown tank for further treatment.

Naphtha and gasoline vapors pass upward through another section containing nine bubble trays, where the naphtha cut is separated from the gasoline. As a third side cut, the naphtha is led through a three-inch line to the third side stripper, where it is further processed in order that the lighter gasoline fractions may be removed through the action of falling downward over the plates and by having superheated steam injected into the mass before it is removed to the condensers and reflux drum. The hot naphtha is picked up by a two-inch Westco turbine pump and discharged back to the main tower as reflux. A Brown automatic temperature controller permits a sufficient amount to pass from the pump to maintain a temperature of 390° F. on the main column below the point where the naphtha is removed. The liquid leaving the reflux drum passes through an additional cooler before being led to the rundown tanks. A Braun tubular section is utilized for this purpose, water being circulated through the shell to cool the product before final disposal. A manifold equipped with Nordstrom plug lubricated valves is installed to facilitate the removal and direction of the flow from the seconndary cooler. Approximately nine per cent of the crude charge is removed and converted into naphtha by this operation; the gravity of the product being 49.5° A.P.I.

The gasoline vapors which have passed successively through the various plates in the tower ascend through an additional six plates to be removed from the overhead through an 18-inch line leading to the vapor-to-crude exchangers. Passing through these units, the partially cooled vapors are condensed in submerged coils in the tank common to the other coils, then flow to the



Motors Serving Pumps Shown on opposite page.



Convenient sampling arrangements in skimming plant of Producers & Refiners Corporation, West Tulsa, Oklahoma.

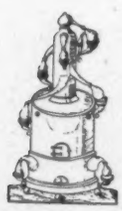
accumulator or reflux drum. A part of this material is picked up by a 1½-inch Worthington centrifugal pump driven by a 10-horsepower Allis-Chalmers 440-volt motor. This is conducted back to the top of the column through a two-inch line, the flow controlled by Brown instruments in order that the top temperature may be maintained at 330° F. Approximately 30½ per cent of the original charge is taken from the tower as a gasoline cut. The hot product from the accumulator tank passes through two sections of Braun enclosed coolers to lower the temperature to prevent losses from the rundown tanks. Tower pressures of 8.5 pounds is sufficient for operating the unit, and to direct the side cuts and gasoline overhead to the proper storage without additional pumps.

One feature of this installation is the economy of operation. Between 58 and 60 cubic feet of gas is required to process each barrel of crude; Dubbs gas and residue from the gasoline recovery plant is utilized for fuel. This consumption is calculated by the engineers of the plant to be about equal to 1.3 per cent of the charging stock fed to the plant. Steam to the amount of .8 pounds to the barrel of oil is required as process steam, while the distillation loss averages nearly 0.5 per cent. One man is all that is required in the operative force.

Only a few times since the installation of this unit have the tubes of the still been turbined. It is found that if at the end of a run, that steam be injected into the tubes, the scouring action of steam will clean the tubes of practically all scale and carbon deposits. As this is injected into the tubes, it flows in the same direction as the crude charge, being picked up in the fuel oil side stripper after passing to the base of the main fractionating tower. It is removed to the dirty charging stock to be processed through the special dehydrator and charging stock cleaner designed and erected under the directions of the plant superintendent, John Cutter, who has made some radical changes in the operation of several units of the refinery.

Below is a typical one-hour report covering the operation of the unit:

	Degrees		Degrees
Charging Stock	39.9 API	Kerosene section	465 F.
Crude to exchangers	180 F.	Naphtha section	390 F.
Crude to Tubes	330 F.	Gasoline section	330 F.
Furnace, N	1030 F.	Dubbs Chg. stock	235 F.
Furnace, C	1000 F.	Super htd. steam	505 F.
Furnace, S	980 F.	Crude meter	54
Flue, N	400 F.	Tower pressure	8½ lbs.
Flue, N	400 F.	Gasoline gravity	60.2 API
Flue, S	420 F.	Stream temp.	104 F.
Flue, S	400 F.	Naphtha gravity	49.5 API
Transfer line	600 F.	Stream Temp.	100 F.
Bottom of tower	535 F.	Kerosene gravity	40.8 API
Distillation Sec.	500 F.	Stream Temp.	116 F.
		Dubbs Chg. stock	25.6 F.



Viscosity Breaker...

Increases Yield of Cracking Stock

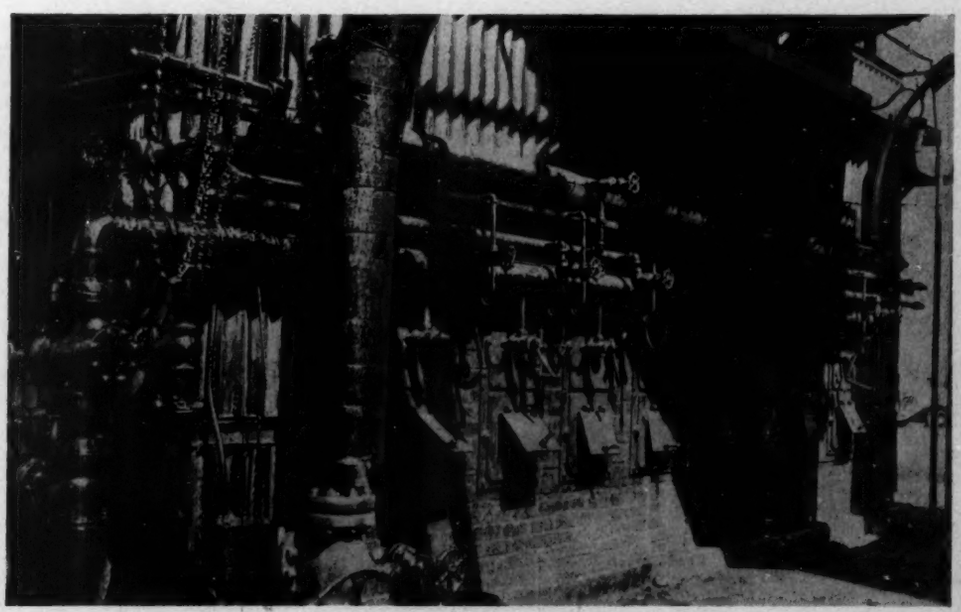
J. C. ALBRIGHT

DURING normal operation, fuel oil approximating 150,000 barrels had accumulated at the plant of the Waggoner Refining Company at Electra, Texas. This oil, with a gravity of 8/10 A.P.I. has been difficult to move, due principally to the condition of the fuel oil market. However, having such a large amount on hand, the management decided to process it so that two products might be obtained, one of which is low gravity gas oil, valuable as a cracking stock, and the other a solidified pitch, brittle enough that it could be passed through ball mills to be used as pulverized fuel. Company engineers have designed for this work a reduction unit, operated at a slight pressure above atmosphere, which has a capacity of 2500 barrels throughput per day.

The unit is compact, and consists of three major portions; pipe still, evaporator column and heat exchangers. The tube still is equipped with eight Alcorn combustion units, each having a three-foot carborundum muffle. Sixty-eight 20-foot tubes are installed, having an outside diameter of 3¼ inches, and an inside diameter of 2¼ inches. Twenty-three of these are installed as roof tubes, 18 as convection and 27 as floor tubes. The roof and sides are covered with Johns-Manville corrugated transite sheeting. The stack breeching extends the full length of the furnace. Sufficient pipe coils are placed in the breeching to furnish superheated steam, which is used in the evaporating column in extracting the gas oil contained in the charge.

The column is 68 inches in diameter and has an effective height of 41 feet. It is supported on a six-foot skirt which provides a total height of 47 feet from foundation to the top outlet flange. Approximately one-third the way up the tower is placed a splash pan. Above, and in the upper half of the column are eight baffles which are designed to break up the ascending vapors and hold back the heavy particles of pitch residuum that is carried upward with the steam used in processing. Bolted cover manholes are placed between each baffle and the next above in order that cleaning of them may be accomplished should coking occur.

Three Southwestern high pressure heat exchangers



FIRING FRONT
Viscosity Breaker

WITH an accumulation of relatively heavy fuel oil in stock, Waggoner Refining Company decided to erect a tube still unit designed for viscosity breaker service to process this material.

Through this practice the company secures a yield of 70 per cent gas oil for use as cracking unit charging stock. This, in turn, yields 70 per cent pressure distillate.

The residuum from the operation becomes a solidified pitch, brittle enough to pulverization through ball mills.

The unit is designed for further operation as a naphtha reforming plant after it has served its purpose as a viscosity breaker.

are placed within a steel structure erected near the tower. Each has 550 square feet of exchanger surface and are connected to each other by diaphragm type expansion joints. Below the last exchanger is a Southwestern tube and shell exchanger, utilized as a vapor condenser and gas oil cooler. Beneath this vertical bank of exchangers are the charging and residuum pumps.

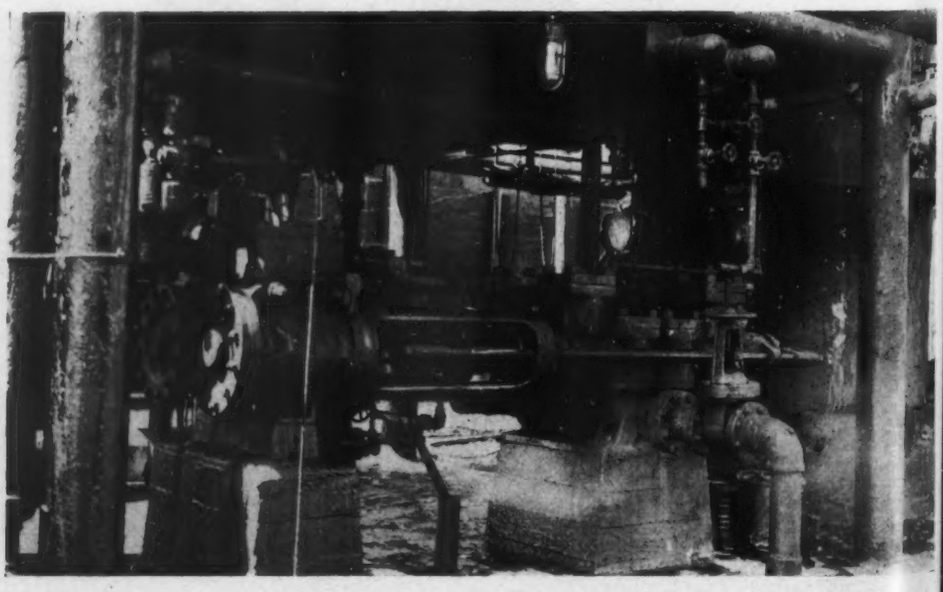
In operation, the charging stock is received from the fuel oil storage at a temperature sometimes as high as 150° F. This occurs when fuel is being pumped out of the same tank in which it is being transferred from the pipe still units in the plant. A 12 by 4 by 12 duplex Fairbanks pump operating under 150 pounds discharge pressure delivers the charge directly to the lower exchanger, connected so that the flow is through the tubes. Passing in series through the three exchangers in counter flow to the overhead stream from the column, the charge leaves the top section at a temperature of 550° F. Passing through an insulated four-inch line, the hot oil enters the roof bank in the furnace, traveling down through the convection bank and then entering the floor tubes. Emerging from the last section of tubes, heated to 900° F., the oil is carried upward in the transfer line to the column. This line enters the shell of the column near the base, but is continued upward inside the tower to a position which provides for a distribution of the material over the splash plate. As the charge is broken up as it leaves this extension of the transfer line, it falls to the compartment in the base of the tower where a spider is placed which distributes the superheated process steam.

COLUMN OPERATION

Process pressure on the column is an average of 15 pounds above atmosphere, which is sufficient to remove the heavy residuum from the tower. The removal line is located at the bottom and a portion of the gas oil vapors is carried out with the residue. Originally the residuum pump was connected directly to this line, but a small portion of coke formed in the base of the column which fouled up the valves in the fluid end of the pump. To remedy this condition, a settling tank was installed. This tank was made from an old Dubbs reaction chamber, set in a horizontal position near the pumps. It serves two purposes, one as a surge tank for pump suction, and to trap all solidified matter coming from the tower. Two baffles are placed in the lower half of the drum over which the residuum must travel as it passes through the tank.

In removing the residuum, a Union simplex outside piston packed pump, size 10 by 3½ by 10, with a forged steel hydraulic fluid end, is utilized. Four large earthen storage tanks have been constructed in which this re-

CHARGING PUMP
for the Viscosity Breaker System



siduum is placed. As it is pumped out at a temperature of around 700° F., it is quite fluid and flows readily over the surface of the pits. As it cools it forms a hard brittle pitch which breaks easily into finely divided particles. Provisions have been made to remove the accumulated pitch from the pits with a drag line shovel dividing dikes have been made wide enough that the shovel may be moved around each pit. Steam lines are connected to several points in the residuum disposal system so that the various lines may be blown free from pitch immediately after the unit is shut down.

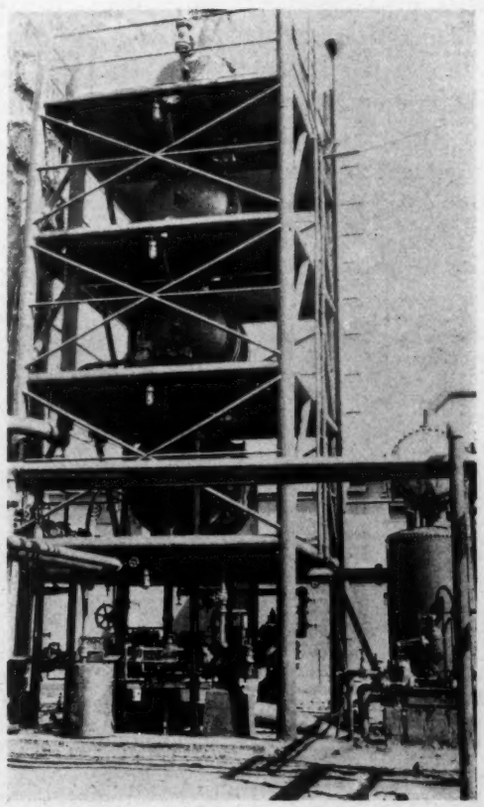
The gas oil vapors driven from the heated stock in the evaporating column pass upward through the eight baffles which retard the passage of any pitch which may be mechanically carried over by the velocity of the vapors and the process steam. Self refluxing is obtained within the tower without the necessity of pumping liquid back. No provisions are incorporated in the unit for top temperature control but it automatically remains close to 750° F. This vapor is removed as an overhead stream through a six-inch line which was fabricated in the plant into a long overbend to take care of stresses within the pipe. Flanged to the top of the upper exchanger, this pipe delivers the vapors to the shell through which it passes in series to each of the three sections in turn. Below the last, or lowest section is placed a Southwestern tube and shell condenser through which the vapors pass before being received in the accumulator. This cooler-condenser has 1000 square feet of exchanger surface, and the distillate emerges at about 150° F. Near this unit the vertical accumulator tank is set from which the distillate is removed by a six by four by six Gardner steam pump, which delivers it to the designated storage tank.

The distillate, or gas-oil has a green color, with a gravity ranging from 14 to 15 A.P.I., and has a cold test around 60° F. The plant has a capacity of 2500 barrels of heavy fuel oil daily, and from this charge is recovered 70 per cent gas oil. From tests conducted and from cracking runs, an average of 70 per cent of pressure distillate is normally recovered.

Throughput and temperatures are carried automatically, Foxboro instruments are set on the control board near the pumps. A Mason regulator was installed in the fuel line which admits gas to the Alcorn combustion units as needed. The thermometer is set in the transfer line and through the Foxboro controller recorder operates the fuel valve. One man is detailed to operate the unit but his duties also require his attention to two shell stills beside which this reduction unit is installed.

This unit was designed and built with a dual purpose. First to reduce the large stock of accumulated low gravity fuel oil, and after this has been processed, to be utilized as a re-forming plant in the processing of straight run gasoline into high knock rating motor fuel. Oversize high pressure high temperature rating exchangers and heavy pipe was used throughout with this idea in mind, so that only a minimum amount of redesigning must be done when it is placed in operation for this purpose.

Four Southwestern high pressure exchangers and condensers set in viscosity breaker at Waggoner Refining Company's plant at Electra, Texas. Upper three are exchangers fuel charge against vapors while lower is straight water cooled condenser.



Aniline Solubility of Gasoline As Index of Anti-Knock Value

C. T. NUNN
Chief Chemist, Misko Refineries

IT was the writer's privilege to be associated with a vaporphase experimental plant a few years ago, during which time he came into contact with a goodly number of representatives of some of the major oil companies in the United States. At that time, critical solution temperatures of gasoline and aniline were in use in that laboratory as a control test. Indicating the extent of cracking and anti-knock value. The test was more or less discounted by the visiting chemists and research men, who contended that it was only very broadly indicative. Since that time, however, the writer has had occasion to check aniline numbers against each other, against engine tests, and against operating conditions of the plant with which he is now associated. From this work the conclusion is drawn, that given a cracking charge constant as to base, this test may be used to evaluate anti-knock properties of a gasoline, and that this evaluation is reproducible and accurate.

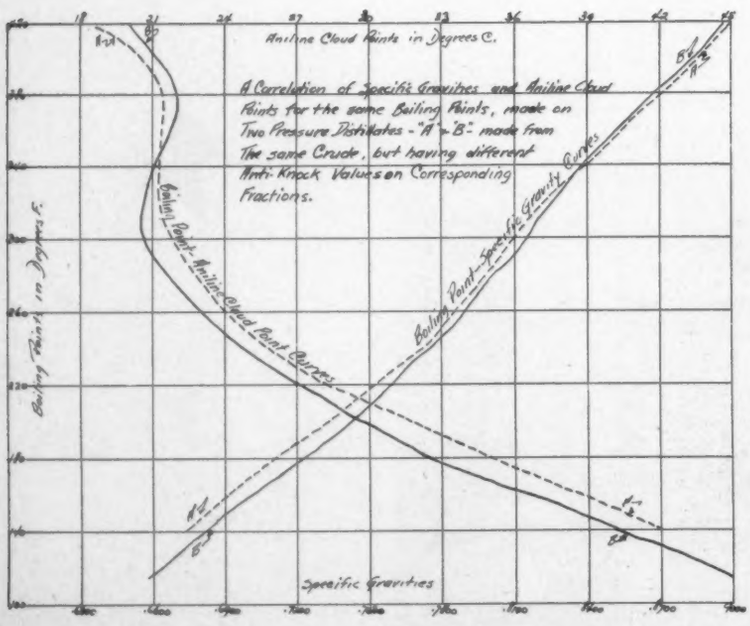
It is, of course, necessary at first, to correlate aniline solution temperatures to actual engine tests, in order to find the relation existing between the two. After this has been done, with gasolines that represent as wide a divergence of anti-knock values as possible, plant procedure can be controlled to produce any required octane number, within, of course, the range possible for that particular plant.

A test, much simpler than the determination of the actual critical solution temperature has been devised, and found to be just as accurate and reproducible. This method follows:

In a small test tube, preferably 25 ml, place equal volumes of C. P. Aniline and the gasoline to be tested. In the writer's laboratory, 10 ml of each are used. These volumes should be accurately measured, either with a pipette or burette, and the gasoline and aniline should be at approximately the same temperature. This test tube should be immediately stoppered with a cork through which has been tightly secured a thermometer, and water jacketed with a larger test tube. Pyrex test tubes are much safer to use. The test tubes are then heated to produce a clear solution of the gasoline and aniline, or if already clear at room temperature, the solution should be cooled to turbidity. The temperature of the solution, as recorded by the thermometer should be read at that point at which turbidity commences. This temperature is called the aniline cloud point in this laboratory.

This method is much easier and requires considerably less time than an actual critical solution temperature,, and, because the results are purely relative and depend on a predetermined factor for translation to terms of octane numbers, it is quite as accurate. Because every plant must work out its own translating factor, it has not been considered necessary to present that in use at this plant.

The accompanying graph shows the close agreement between specific gravities and aniline cloud points for the same boiling ranges of different octane number gasolines made from the same crude, and has been presented because of the wide acceptance of the specific gravity-boiling range relation as an index to anti-knock value.

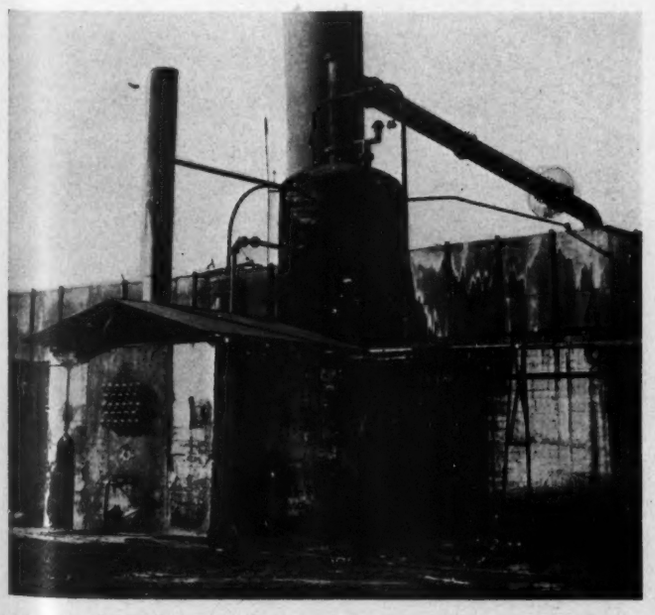

Aniline Cloud Points in Degrees C.
A Correlation of Specific Gravities and Aniline Cloud Points for the same Boiling Points, made on Two Pressure Distillates - "A" & "B" - made from The same Crude, but having different Anti-Knock Values on Corresponding Fractions.
Boiling Point-Aniline Cloud Point Curves
Boiling Point-Specific Gravity Curves
Boiling Point in Degrees F.
Specific Gravities

Dehydrating Unit and Dubbs Blow-Down

PRODUCERS & REFINERS CORPORATION, West Tulsa, has installed a system for the dehydration of oil and for preventing the tarry residuum from blowing over the plant when the Dubbs units are brought off stream. When some of the old equipment had been removed, one of the old furnaces was utilized in which a small pipe still was placed, through which the dirty oil is passed in removing the water. Above this unit two receivers were placed, one of which was made from an old Dubbs reaction chamber and is used when a considerable amount of oil is to be processed in removing water, while the other is a small drum used only when only a few barrels are to be passed through the unit.

The large receiver is equipped with a 20-inch vapor line made of light pipe leading to a series of submerged pipe coils in which the light fractions removed from the oil and the water vapors are condensed. The small drum has an individual line leading to the same series of condensers and the condensate is received in a common run tank or accumulator set on the ground near the unit.

This unit is utilized when the Dubbs cracking units are being brought off stream in the first part of the operation. All the pressure is relieved through this apparatus, the pipe still being by-passed, at such times. In the second phase of the blowing down operation, that is, when the steam is being introduced, the second unit is utilized. This unit is composed of a light bottomless floating tank suspended in the tar pit under a steel framework. A hook is fastened to the cover of this receiver to which a block with wire lines are attached. This is done for two reasons; one, to prevent the tank from resting on the bottom of the pit, and second, to raise it clear of the slops when cleaning is necessary. A vapor line leading from a water seal attached to the tank is connected to a submerged section of condensing coils placed in a tank near the unit.



Dehydrating and Dubbs Blow-Down in Plant of Producers & Refiners Corporation, West Tulsa, Oklahoma.

Dubbs Blow-Down Apparatus, Showing Line Leading from Floating Tank to Condenser Sections.

The liquid residuum coming from the cracking units is trapped in this tank, preventing its being blown over the plant. The light fractions and steam are carried over through the vapor line to the condensers. The water from the accumulator is drawn to the drains while the recovered distillates are passed back for processing through the stills.

Spent Caustic Reclaimed By Concentrating

CAUSTIC solution which is used in the treatment of vapors from the fractionating towers, or that injected into the liquid streams from the condensers is often drawn from the run down tanks into the sewer or drains and permitted to flow away. At the Kettle Creek Refining Company plant at El Dorado, Arkansas, the treating solution is saved, concentrated and used a number of times, thus securing the full benefit of the caustic remaining in solution after treating gasoline and other distillates.

Treating at this plant with caustic solution is carried out in the liquid phase. It is pumped through a distributing system which leads to the receiving house with individual lines entering the look boxes through which the kerosene, naphtha and gasoline are carried to the run down tanks. The distillates and caustic after entering the tanks are pumped to the agitator. The caustic solution diluted with water which has passed over the separators, being heavier than the petroleum fractions, is of course picked up by the pumps first and discharged to the agitator. The distillate coming next is forced through the solution which has settled to the

Three Caustic Reconditioners or Concentrators in Plant of Kettle Creek Refining Company.

Pipe Over Look Box Shows Method of Feeding Reconcentrated Caustic Back into the Stream.

bottom of the agitator where it receives its second contact with the solution.

Three horizontal tanks near the agitator which had been used as chemical storage, were converted to caustic reclamation units by placing steam coils inside the shell, occupying about one-third of the interior. The solution is drained from the base of the agitator to either of the tanks not in operation. Live steam from the boiler room led through insulated headers to the treating plant is turned through the coils in the tank and permitted to remain until the solution has been concentrated to the desired strength. The manholes in the upper side of the tanks remain open so that the steam coming from the boiling solution may escape. Either one or all three tanks may be in operation at the same time with three stages of concentration in process.

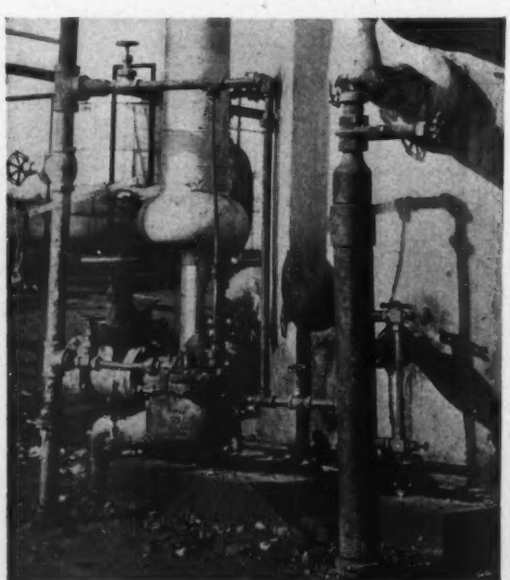
The caustic solution when first introduced to the look box stream is around eight gravity, and when the concentration reaches five degrees, it is considered strong enough to remove to the chemical storage tank to be brought up to operating strength by the addition of fresh caustic and placed in the circuit again.

Covering a period during which 27,325 barrels of gasoline and 5050 barrels of kerosene were manufactured, only 4350 pounds of caustic was consumed in treating. This shows that the treating needs were approximately two ounces of caustic to the barrel of gasoline, or approximately 330 gallons to the pound of the original caustic. No additional labor was necessary to operate the concentrators, as the plant treator was able to handle this apparatus in addition to his regular duties.

Still Steam Trap Does Double Duty

REQUIRING a three-quarter-inch steam trap to do double duty was the idea when this device was hooked up to serve two points in steam lines on the still in the Trosper Park gasoline plant of Wirt Franklin, Cromwell Drilling Company and Indian Territory Illuminating Company, Oklahoma City field.

Some condensation was present in the live steam at the point of introduction to the multi-tubular heating elements as well as at the point where the process steam was injected. To eliminate this water, a three-quarter trap was hooked up so that it drained both places coincidentally. A two-inch line was connected to the live steam line placed in the top section of heating elements, extending downward and also being utilized as a line through which the condensed water is led away to the boiler hot well. A tee was inserted a short distance above the ground, and below this connection a gate was placed to serve as a shut off. Connections leading from the tee above this gate were tied into the trap and the outlet connected to the line below the gate. A tee was placed in the line before the process steam was introduced to base of the still, and below that point, the two-inch was swedged to four-inch; a piece about three feet long with a cap on the lower end serving as an accumulator or reservoir for the condensation. Connecting this drum to the inlet side of the trap serving the other line forced the trap to drain the condensate from two points at the same time. Clean, dry, saturated steam is always available for both purposes and eliminates the water content of the lean oil leaving the still.



Steam Trap Connections at the Still in the Plant of Wirt Franklin in Trosper Park, Oklahoma City.